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NMR Data on Protonated Benzazoles

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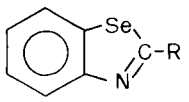
NMR parameters referring to 2-protons and 2-methyl protons provide some comparison in the series of benzoselenazole (I), benzothiazole (II) and benzoxazole (III). Furthermore, when protonation occurs in these molecules, some interesting modifications of properties of the 2-position arise.

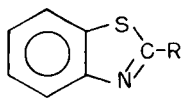
Chemical shift values of 2-methyl protons in benzazoles in carbon tetrachloride solution have recently been reported (1). In this work we refer to chemical shift and $J_{C^{13}-H}$ values in benzazoles and 2-methyl benzazoles, detected both in inert (carbon tetrachloride) and acidic medium (trifluoroacetic acid).

In Table I are summarized chemical shift and $J_{C^{13}-H}$ values which we have observed in our measurements on benzazoles.

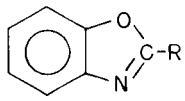
A comparison of the three series shows that the signals for the 2-protons and 2-methyl protons come consistently at lower field in the benzoselenazoles and benzothiazoles than in the benzoxazoles. The deshielding effect of the heteroatom is opposite to the order of electronegativity: consequently it is in the same way as the tendency of the heteroatoms to contribute electrons to cyclic resonance, and therefore as the tendency of the compounds to sustain an induced ring current. Chemical shift value of 2-H in benzoselenazole appear to be unusually high if compared with relative electronegativity value of selenium. Protonation of these molecules is accompanied with unusually high chemical shift values for 2-H and 2-CH_3 protons: this is not unexpected in terms of the relatives resonance stabilized cations. The gap between chemical shift values in benzazolium ions is lowered, benzoxazoles being more affected on protonation than benzothiazoles and benzoselenazoles.



(I)



(II)



(III)

TABLE I

$J_{C^{13}-H}$ and Chemical Shift (cps) Values for 2-H and 2-CH_3 Protons in Benzazoles

Compound	-R	J Calcd. (b)	Coupling Constants		Chemical Shifts	
			Neat	CF_3COOH	CCl_4	CF_3COOH
I	-H	-	214.0	216.0	591.5	666.5
I	$-CH_3$	-	130.5 (a)	134.8	168.78 (c)	196.0
II	-H	206.5	211.0	215.0	536.5 (d)	611.5
II	$-CH_3$	-	130.6	134.2	167.56 (c)	195.0
III	-H	227.0	231.5 (a)	243.0	483.0 (d)	590.0
III	$-CH_3$	-	131.0	135.0	155.88 (c)	189.2

(a) Samples added to the least volume of carbon tetrachloride to obtain liquid substances at room temperature. (b) See Ref. (4). (c) Values taken from Ref. (1). (d) See also Ref. (8).

$J_{C_{13}-H}$ for 2-CH_3 protons in benzazoles are essentially not different, but their values provide evidence for a strongly electron withdrawing character of the heteroaromatic substrate. The 2-CH_3 protons should be able to exchange with deuterium, as found in 2-methyl benzothiazole and 2-methyl benzoxazole by Abramovich (2). On protonation $J_{C_{13}-H}$ values increase and are again essentially the same, indicating a greater electron withdrawing character of the "benzazolium" substrate.

The observed coupling constants are in agreement with calculated constants using Malinowsky's rule (3,4). Available literature data on isotopic exchange in 2-H benzazoles show that benzoxazole reacts 16 times faster than benzothiazole (5). These results appear to be opposite to the order of acidity obtained on the basis of chemical shift values. An analogous statement was made by P. Haake and W. B. Miller in a comparison of thiazoles and oxazoles (6). $J_{C_{13}-H}$ for 2-H benzazolium ions indicated an unusually high acidity of these protons due to the electron withdrawing character of "benzazolium" substrate.

EXPERIMENTAL

Materials.

The investigated 2-methyl benzazoles were prepared and purified by the procedure given in reference (1). 2*H*-Benzoselenazole was prepared and purified as indicated in reference (7). 2*H*-Benzothiazole and 2*H*-benzoxazole were purchased commercially and purified by redistillation under reduced pressure.

NMR Measurements.

Chemical shift values were recorded on a Varian A-60 spectrometer in a 2.5% solution in carbon tetrachloride or trifluoroacetic acid with tetramethylsilane as internal standard. Accuracy of the measurements was estimated as ± 0.6 cps.

$J_{C_{13}-H}$ values were recorded on pure substances or by dissolving 5×10^{-3} moles of benzazole in 1 ml. of trifluoroacetic acid. Accuracy of the measurements was estimated as ± 1 cps for 2-CH_3 derivatives and ± 2 cps for 2-H derivatives. Spectra of benzoxazoles in trifluoroacetic acid were recorded immediately after the dissolution.

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