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THE NMR SPECTRA OF BASIC PRIMARY ALCOHOLS

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It is known that many alcohols may be classified by observing their spectra in dimethylsulphoxide (DMSO) (1). In the latter strong hydrogen bonding to the solvent shifts the hydroxyl resonance downfield and reduces the rate of proton exchange so that spin-spin coupling of the hydroxyl proton may be observed. This situation (2) does not always hold however, as the method has been found unreliable for a number of alcohols having strong electron-withdrawing substituents close to the hydroxyl group. It is concluded (2) that structure and perhaps geometry are important as well as electronegativity.

The absence of the expected spin-spin coupling between the hydroxyl and methylene protons of o-aminobenzylalcohol in DMSO prompted us to look into the problem further. It is apparent that the amino group of o-aminobenzylalcohol is sufficiently basic to accelerate the hydroxyl proton exchange rate so that loss of multiplicity of both hydroxyl and methylene resonances occurs.

The NMR spectra of a number of alcohols containing basic centres and of benzyl alcohol in the presence of equimolar quantities of bases of varying pKa have been examined. The results are shown in the following Table.

No.	Alcohol[a]	Added Base	pKa[b]	Spin-spin coupling -CH$_2$OH
1	Benzyl alcohol			Yes
2	Benzyl alcohol	o-nitroaniline	-0.28	Yes
3	Benzyl alcohol	m-nitroaniline	2.45	Yes
4	Benzyl alcohol	phthalazine	3.47	partial[c]
5	Benzyl alcohol	aniline	4.62	No
6	o-Nitrobenzylalcohol			Yes
7	o-Aminobenzylalcohol			No
8	3-Hydroxymethylpyridine			No
9	5-β-Hydroxy-4-methylthiazole			No
10	γ-Dimethylaminopropanol			No
11	3-Hydroxymethylpyridinium methiodide			Yes
12	3-Hydroxymethylpyridinium methiodide	o-nitroaniline	-0.28	Yes
13	3-Hydroxymethylpyridinium methiodide	pyridine	5.23	No
14	o-N,N-dimethylaminobenzyl alcohol			No
15	[(o-Hydroxymethyl)phenyl]trimethyl ammonium iodide			Yes

Footnotes to Table

[a] All spectra were obtained as 10% $^{w}/v$ in DMSO solutions on a Varian A60 instrument.

[b] Taken from the manual on Ionisation Constants by Albert and Serjeant (1962). These values are those for aqueous solutions and are not intended to be an indication of the absolute basicity in DMSO solutions.

[c] Broadening of multiplets, coupling just observable.

It can be seen from the Table that when equimolar aniline is added to benzyl alcohol coupling of the hydroxyl and methylene protons is removed. When aniline was added to benzyl alcohol in less than a molar equivalent, a gradual broadening of the respective multiplets was observed. On the addition of weaker bases such as ortho- and meta- nitroanilines, coupling occurred without any noticeable broadening. The limiting case appeared to be phthalazine where coupling was just discernable on the broadened resonances.

Entries 7 to 10 in the Table are alcohols containing a sufficiently basic centre to facilitate rapid proton exchange of the hydroxyl, thus causing loss of multiplicity. No coupling occurs with 3-hydroxymethylpyridine in contrast with its methiodide in which the basic centre has been removed by quaternisation. A similar situation exists with o-N,N-dimethylaminobenzyl alcohol and its corresponding methiodide, /(o-hydroxymethyl)phenyl/trimethyl ammonium iodide.

It can be seen from this limited study that the presence of basic centres in alcohols must be taken into account when interpreting their spectra in DMSO solutions.

References

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2. J. G. Traynham and G. A. Knesel, ibid., **87**, 4220 (1965).