

Hydrogen Bonded Carbanions directly observed by ^1H N.M.R. and I.R. Spectroscopy

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Intramolecular hydrogen bonding between the fluorenyl and indenyl anions and the hydroxy groups of 9-(3-hydroxy-1,1,2,3-tetramethylbutyl)fluorene-9-ide (1) and 3-(3-hydroxy-1,1,2,3-tetramethylbutyl)inden-3-ide (7), respectively, in dimethyl sulphoxide has been observed by ^1H n.m.r. and i.r. spectroscopy.

In the mechanism of proton transfer reactions of carbon acids with bases, hydrogen bonded carbanions are postulated as intermediates. However, such species have not been accessible for direct observation since under the conditions used they are unstable. Consequently, knowledge about their properties is meagre as is the knowledge in general about solvation of carbanions by hydrogen bonding.¹

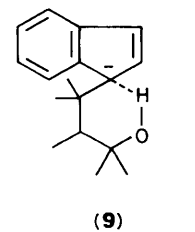
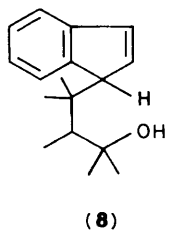
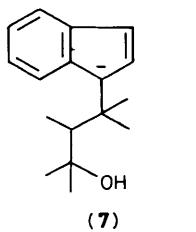
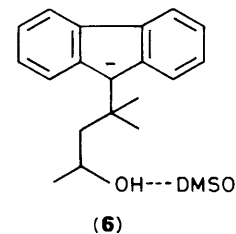
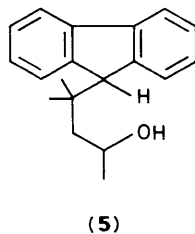
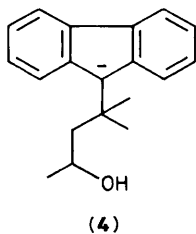
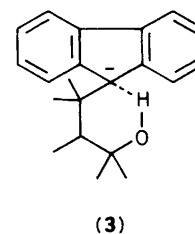
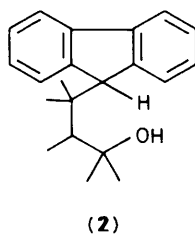
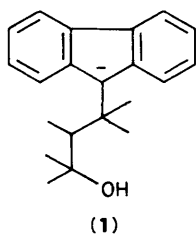
To our knowledge there have been no reports prior to this on direct observations of specific hydrogen bonding to carbanions *i.e.* of the type $\text{C}^- \cdots \text{H}-\text{X}$, where X is an electronegative atom. But recently evidence for intramolecular C-H-C bonds in carbanions of [1,1]ferrocenophanes has been published² and the strength of some hydrogen bonds to carbanions in the gas phase has been measured.³ There also exist some reports on solvent bulk hydrogen bonding of stable carbanions in hydroxylic solvents.⁴

The chemical shift of the hydroxy proton in methanol added to fluorenyl anion in dimethyl sulphoxide (DMSO) remains the same as that in pure DMSO over a large concentration interval. Since significant hydrogen bonding of methanol to fluorenyl anion is expected to cause some shift of the hydroxy proton, it is concluded that no significant hydrogen bonding to the fluorenyl anion is present. Obviously the delocalized carbanion fluorenyl anion is not a powerful enough hydrogen

bonding reagent to be able to compete with the solvent DMSO for the methanol molecules.

The ^1H n.m.r. spectrum at 400 MHz of mixtures of anion (1) and its precursor 4-(fluorenyl)-2,3,4-trimethylpentan-2-ol (2) in DMSO on the other hand showed two broad hydroxy proton signals. The one in (1) appeared 0.95 p.p.m. upfield of that of (2). This suggests that the hydrogen bond between the OH and DMSO upon formation of the anion has been exchanged for a $\text{C}^- \cdots \text{HO}$ bond [*cf.* structure (3)]. The 0.95 p.p.m. upfield shift could partly be ascribed to a change in hydrogen bond character and partly to shielding of the proton by ring currents in the fluorenyl anion. Fourier transform (F.t.) i.r. spectra of the mixtures strongly support these conclusions. Thus, the OH stretching frequency shifts 75 cm^{-1} to lower frequency on going from (2) to the anion (1). The stretching band of (1) was found to be considerably broader than that of the precursor (2).

In contrast ^1H n.m.r. spectra of mixtures of anion (4) and its precursor 4-(fluorenyl)-4-methylpentan-2-ol (5) showed only *one* common broad OH signal which broadened but underwent only a very small shift upon increasing the fraction of anion. At 100 mol% anion the OH signal had disappeared in the base line noise. Furthermore F.t. i.r. measurements on



the mixtures showed no significant difference between the OH stretching frequencies and band widths of (4) and (5). These results indicate that no significant fraction of $C^- \cdots HO$ bonds was formed and that ion (4) may be described by structure (6).

Evidence for $C^- \cdots HO$ bonds has also been obtained in studies of mixtures of (7) and its precursor 4-(inden-3-yl)-2,3,4-trimethylpentan-2-ol (8) by 1H n.m.r. spectroscopy at 100 MHz in DMSO [*cf.* structure (9)]. Two separate OH proton signals from (7) and (8), respectively, were observed. The OH proton in (7) appeared 0.53 p.p.m. upfield of the one in (8). The OH proton signal from (7) is much sharper than the corresponding one originating from (8). This indicates that the proton in the $C^- \cdots H-O$ bond of (7) is less prone to undergo exchange than the DMSO-hydrogen bonded OH proton in (8). I.r. studies of the mixtures revealed a 74 cm^{-1} OH stretching frequency shift towards lower frequency on going from (8) to (7). Furthermore, no significant difference in the band width of the signals from (7) and (8), respectively, was observed in contrast to the observations with mixtures of (1) and (2). These results suggest structure (9) as a representation for ion (7).

The results reported above for ions (1) and (7) seem to constitute the first direct evidence for $C^- \cdots HO$ hydrogen bonds and specific solvation of carbanions by hydrogen bonding.

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