

Hydrogen Bonding of Fluorenone by a Hydroxy Proton Directly Observed by UV, NMR and IR Spectroscopy

Ian McEwen, Mats Rönnqvist and Per Ahlberg*

Department of Organic Chemistry, University of Göteborg, S-412 96 Göteborg, Sweden

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Results and discussion

The two carbanion diastereoisomers **1** and **2** of 3,4-dimethyl-4-(9-fluorenyloxy)pentan-2-ol were designed to be used in our studies of hydrogen bonding to carbanions.^{1,2} They were prepared from the diastereoisomeric precursors **3** and **4** of 3,4-dimethyl-4-(9-fluorenyloxy)pentan-2-ol, respectively, in dimethyl sulfoxide (DMSO) with dimethylpotassium. Fig. 1 shows parts of the UV spectra of the carbanions **1** and **2**, i.e., the π - π^* transitions for their fluorenone moieties are displayed, respectively. The 10 nm difference between the maxima is suggested to be due to intramolecular hydrogen bonding in the carbanion **1** and the absence of intramolecular hydrogen bonding in **2**. This conclusion is strongly supported by the following findings.

The space structures of **1** and **2** were revealed by ¹H NMR studies, i.e., by the NOESY spectra obtained in DMSO-*d*₆. In the spectrum of **1**, the crosspeaks H-6/H-2 and H-1/H-3 were of similar size (Fig. 2). This is consistent with the suggested structure of **1a** shown in Scheme 1 (arrows indicate NOEs), i.e., we are dealing with the diastereoisomer consisting of the (2*S*,3*R*)/(2*R*,3*S*) pair. In the spectrum of **2** on the other hand, the crosspeak H-6/H-2 was much smaller than H-1/H-3, indicating the structure **2a** shown in Scheme 1, i.e., the diastereoisomer consisting of the (2*R*,3*R*)/(2*S*,3*S*) pair. In this structure, the OH group is pointing away from the fluorenone moiety. Rotation around the C-2,C-3 bond forces the OH group to point towards the carbanion, and such a conformer **2b** is expected to show a larger H-6/H-2 crosspeak. Presumably, conformation **2a** is favoured over **2b** because of the steric interactions in the latter conformer of the methyl group H-1 with the methyl groups H-6 and H-5.

IR investigations by FT IR of the OH stretching frequencies of the compounds **1**–**4** gave the following results.

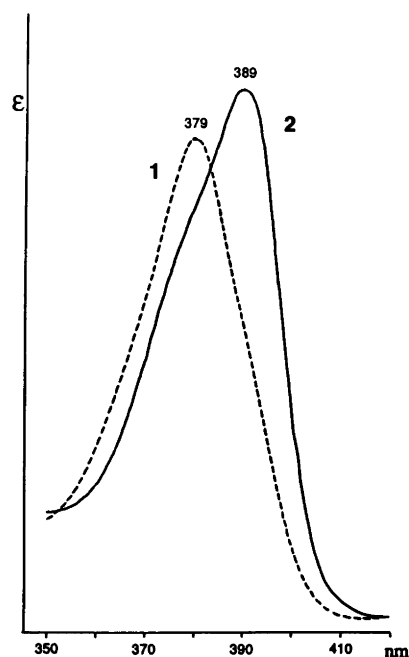


Fig. 1. Electronic absorption spectra of the potassium carbanions (ca. 0.75 mM) **1** (----) and **2** (—) in DMSO at ambient temperature.

The OH stretching band of the carbanion **1** shifted to lower frequencies relative to the corresponding band of the precursor **3**, i.e., from 3375 to 3292 cm^{-1} . Conversely, the OH-stretching band of the other carbanion diastereoisomer **2** shifted to higher frequencies relative to the corresponding band of **4**, i.e., from 3384 to 3414 cm^{-1} .

The NMR, IR and UV results taken together suggest that in carbanion **1** the OH group is intramolecularly hydrogen-bonded to the fluorenone. Thus, the 83 cm^{-1} IR-shift to lower frequencies of the OH band of **1** compared with that of **3**, which is intermolecularly hydrogen-bonded

* To whom correspondence should be addressed.

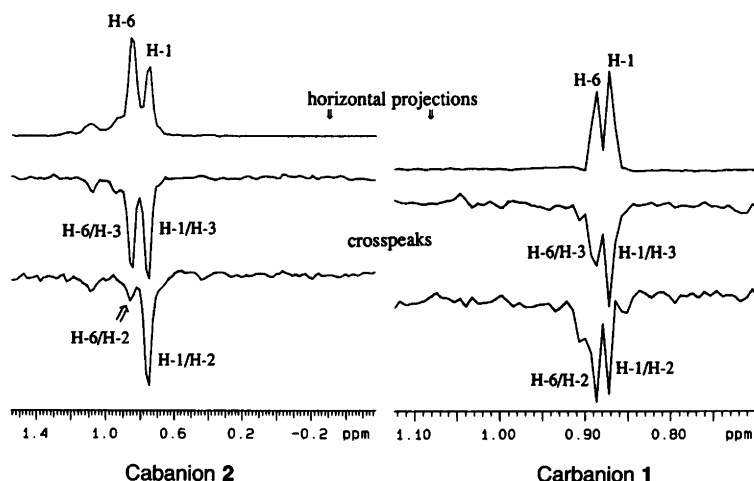
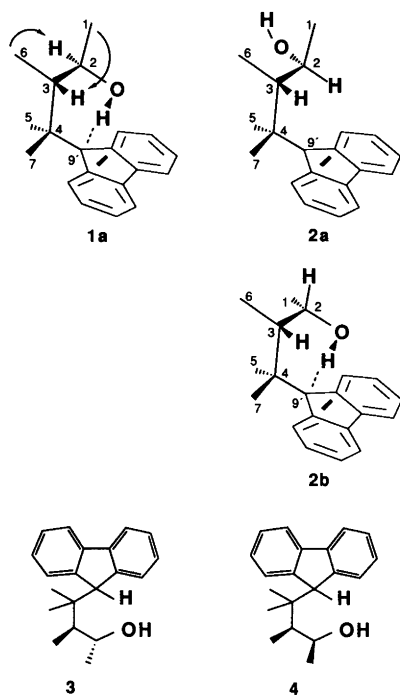


Fig. 2. Traces (or skyline projections) extracted from two phase-sensitive NOESY spectra at 21 °C.



Scheme 1.

to DMSO, reflects the difference in character of the two hydrogen bonds. The hydroxy group in carbanion **2** is concluded to be intermolecularly hydrogen-bonded to DMSO as is the precursor **4**.

We conclude that the 10 nm difference in π - π^* transition frequencies of the fluorenides in **1** and **2** is caused by the specific solvation of the fluorene in **1**, i.e., the intramo-

lecular hydrogen bonding. Such an interaction is expected to cause a hypsochromic shift.

It is interesting to note that the 10 nm UV blue-shift, suggested to be caused by the hydrogen-bond perturbation of the fluorene carbanion, is similar in size to the shift observed by Hogen-Esch and Smid³ for unsubstituted fluorene interacting with Cs⁺ (9 nm) or K⁺ (11 nm) in contact ion pairs in tetrahydrofuran (THF). It has also been reported that the delocalized fluoradenide ion shows a blue-shift in UV of 12 nm (from 388 nm to 376 nm) when aprotic solvents such as THF and DMSO are substituted for protic solvents such as methanol.⁴ Greifenstein and Pagani⁵ have also reported similar blue-shifts in pentadienide derivatives upon addition of water to a solution of the carbanion in DMSO. These shifts were interpreted in terms of hydrogen bonding of the bulk solvent to the carbanion.

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