Fluorenyl-lithium: Direct Evidence for Ion Pairing Phenomena in Solution by ^{6}Li, ^{1}H Heteronuclear Overhauser Effect Spectroscopy (HOESY)

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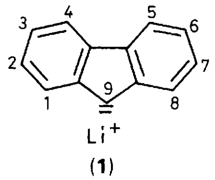
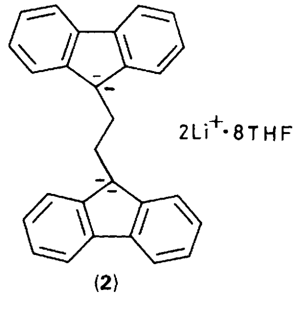
^{6}Li,^{1}H HOESY reveals details of fluorenyl-lithium ion pairing; cross-peaks indicate that the Li$^+$ environment and its interactions with the carbanion depend on the conditions.

The concept of ion pairs, originally introduced by Bjerrum[1] and developed in more detail by Fuoss[2] and Winstein,[3] has been widely applied in organic chemistry.[4] Many spectrometric techniques[4—18] have been employed to investigate ion pair equilibria of alkali metal salts of highly delocalized carbanions in solution. Thus, UV measurements revealed that fluorenyl-lithium (**1**) predominantly forms solvent separated ion pairs (SSIPs) in tetrahydrofuran (THF) at −30 °C.[5] Although the equilibrium is still in favour of the SSIPs at +25 °C,[6] a considerable proportion of contact ion pairs (CIPs) could be detected. These findings were corroborated later by Edlund using ^{13}C NMR spectroscopy.[18] Recently, Müllen[19] described the *X*-ray structure of a bis-fluorenyl-lithium derivative (**2**), which exists as SSIPs in the crystal.

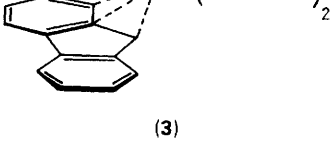
We now describe for the first time the application of a new method which gives more 'direct' insight into ion pair equilibria in solution. ^{6}Li,^{1}H two-dimensional heteronuclear Overhauser effect spectroscopy (HOESY) was introduced by our group for the detection of short lithium–hydrogen distances.[20] In the contour plot of a HOESY spectrum, a cross-peak indicates the proximity (separations less than *ca.* 3.5 Å) of lithium and hydrogen nuclei.



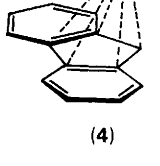
(**1**)



(**2**)



(**3**)



(**4**)

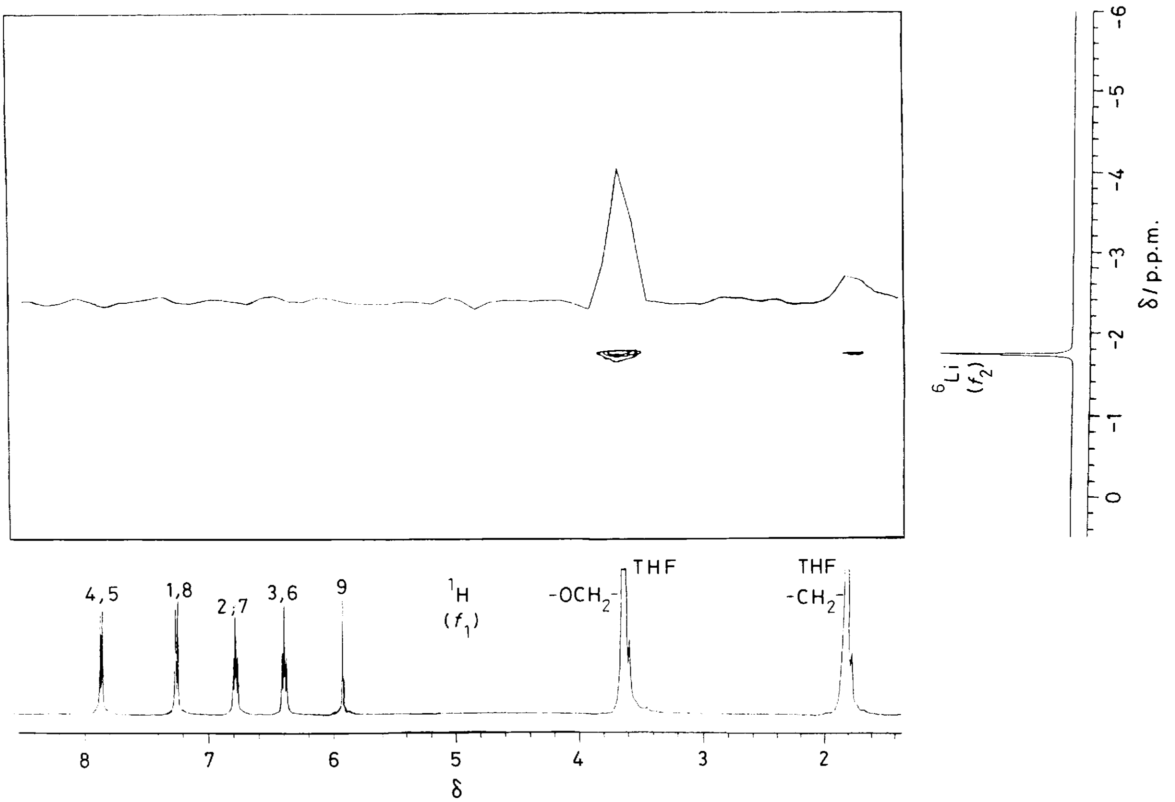


Figure 1. ^{6}Li,^{1}H HOESY (contour plot) of ^{6}Li-fluorenyl-lithium ^{6}Li-(**1**); [$^1H_8$]THF containing crystals dissolved in [$^2H_8$]THF (0.8 M), at −90°, mixing time 2.0 s. Insert: f_1-trace of the ^{6}Li signal.

Crystals of fluorenyl-lithium (enriched with 96% ^{6}Li), obtained by reacting fluorene with n-butyl-lithium in THF, were employed here. When these crystals were dissolved in [$^2H_8$]THF, the HOESY experiment at −90 °C gave a spectrum (Figure 1) showing one intense and one weaker cross-peak between the lithium signal and the ^{1}H resonances of non-deuteriated THF (originally incorporated in the crystal). However, no cross-peaks with the ^{1}H signals of the fluorenyl moiety were detected. This indicates that only the THF ligand is bound to lithium and strongly supports the conclusions of Hogen-Esch,[5] Smid,[4b] and Edlund,[18] that only SSIPs are present under these conditions. The lithium cation is assumed to be tetrahedrally surrounded by four THF ligands and is thus spatially isolated from the carbanion. Similar arrangements are found in a number of crystal structures.[21—27]

According to the earlier work,[4,5,18] considerable amounts of CIPs should be present at higher temperatures. This agrees nicely with our HOESY results at −10 °C. The intense cross-peaks found between lithium and some of the hydrogen atoms of the fluorenyl system (Figure 2) indicate the SSIP/CIP equilibrium to be shifted towards the CIP side.

Fluorenyl-lithium bisquinuclidine adopts structure (**3**) in the solid state[28] with lithium bridging between the 'anionic' carbon C-9 and one *peri*-carbon C-1. However, in addition to the hydrogens attached to these positions, *i.e.* H-1, H-8, and H-9, Figure 2 also reveals a less intense cross-peak between lithium and the hydrogens attached to C-4 and C-5. Hence, fluorenyl-lithium in THF solution obviously adopts a somewhat different structure (**4**) with the cation located almost centrally above the five-membered ring. Moreover, the dissymmetry of the crystal structure vanishes in THF solution to give a (static or time averaged) species of higher symmetry. This is indicated by the presence of only one set of signals in the ^{1}H NMR spectrum for the corresponding positions H-1,8, H-2,7 *etc.* In agreement with the proposed η^5-structure of fluorenyl-lithium in THF solution, no HOESY cross-peaks are found in Figure 2 between lithium and the remote hydrogen positions H-2, H-3, H-6, and H-7.

When the crystals of fluorenyl-lithium containing THF are dissolved in [$^2H_{10}$]diethyl ether, the HOESY-experiment at +8 °C gives the results depicted in Figure 3. A very intense cross-peak is now found between lithium and the H-9 hydrogen atom attached to the 'anionic' carbon C-9. Other cross-peaks involve the protons of THF, even though Et_2O is present in excess.

Hence the lithium cation is less efficiently solvated by diethyl ether, which is a sterically more demanding ligand than THF.[29,30] The SSIP/CIP equilibrium is more strongly shifted towards the CIP side under these conditions than in pure THF solvent, in agreement with Edlund's results.[18] The lithium cation seems to be located more closely to the 'anionic' carbon C-9 than in pure THF. Furthermore, even in the presence of a large excess of diethyl ether, THF competes with the bulk ligand and is bound preferentially to lithium.† This agrees with the findings by Burley and Young[31] on the lithium salt of 1,3-diphenylbut-1-ene; when prepared in tetrahydrofuran, a solution of this salt in diethyl ether still shows solvation of the lithium cation by THF, introduced from the vacuum dried material.

Using ^{6}Li,^{1}H HOESY as a new structural probe, we have demonstrated the correctness of earlier conclusions concerning ion pair phenomena. The results for fluorenyl-lithium,

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† Unfortunately, the limited solubility of (**1**) in diethyl ether does not permit NMR determinations at temperatures lower than *ca.* 0 °C (precipitation).

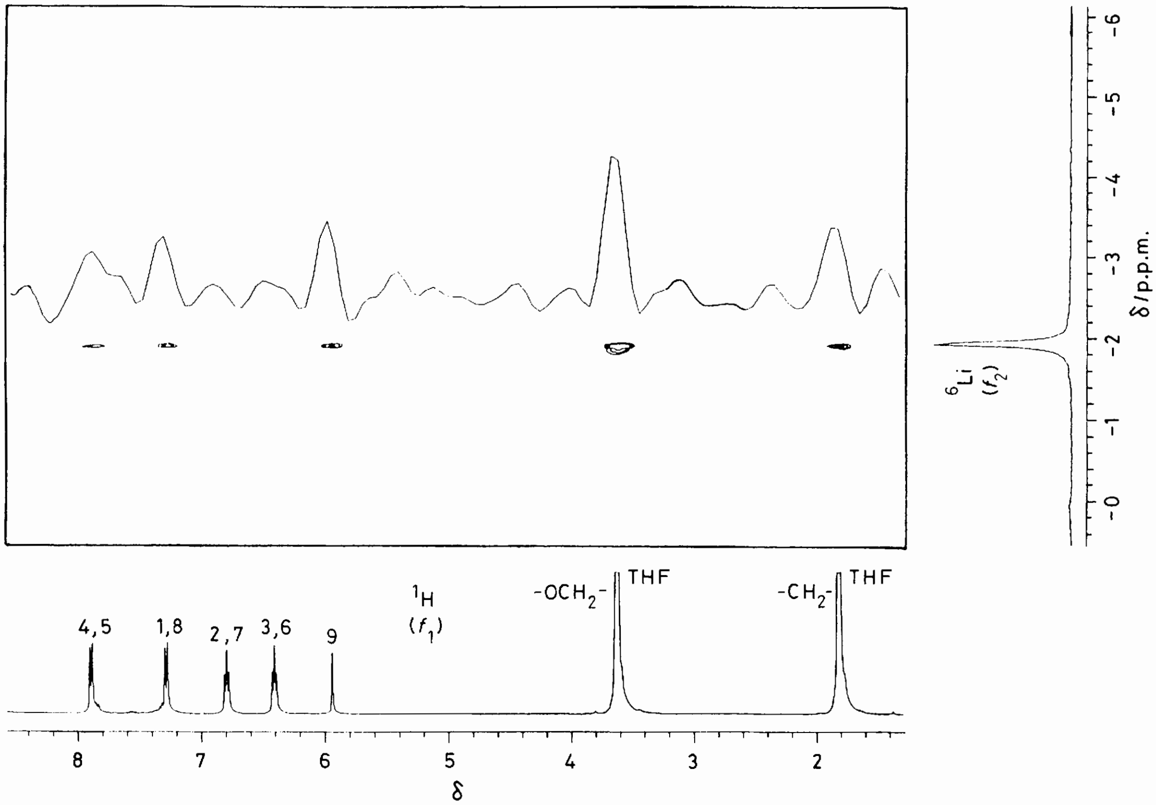

Figure 2. ^{6}Li,^{1}H HOESY, sample as in Figure 1, at −10 °C, mixing time 2.0 s. Insert: f_1-trace of the ^{6}Li signal.

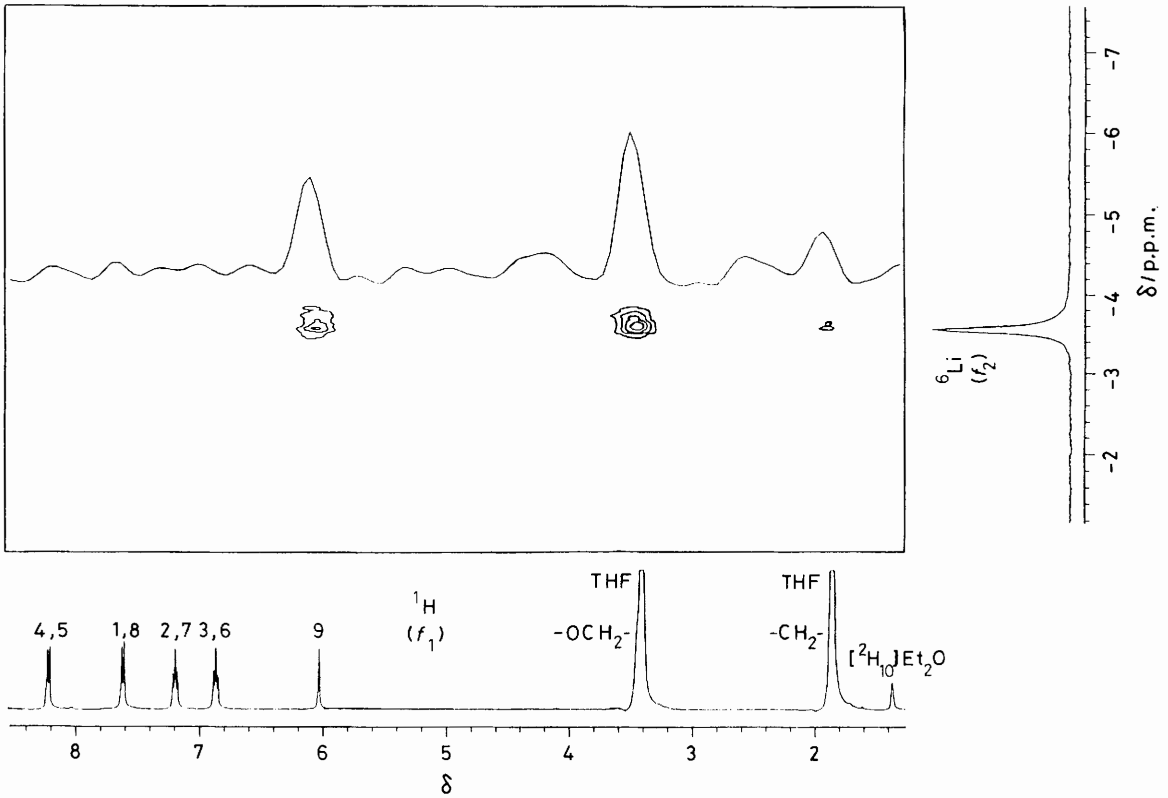

Figure 3. ^{6}Li,^{1}H HOESY of [^{1}H$_8$]THF containing crystals of ^{6}Li-fluorenyl-lithium ^{6}Li-(**1**) dissolved in [^{2}H$_{10}$]diethyl ether (0.6 M) at +8 °C, mixing time 1.8 s. Insert: f_1-trace of the ^{6}Li signal.

obtained by UV,[4—6] ^{1}H[7] and ^{13}C NMR spectroscopy[18] and now with ^{6}Li,^{1}H HOESY agree excellently. Of these, ^{6}Li,^{1}H HOESY reveals the greatest detail concerning the nature of fluorenyl-lithium in solution.

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