Asymmetry of the First directly observed Intramolecular [C–H–C]$^-$ Hydrogen Bond in the Carbanion of [1.1]Ferrocenophane Demonstrated by Dynamic N.M.R. Spectroscopy

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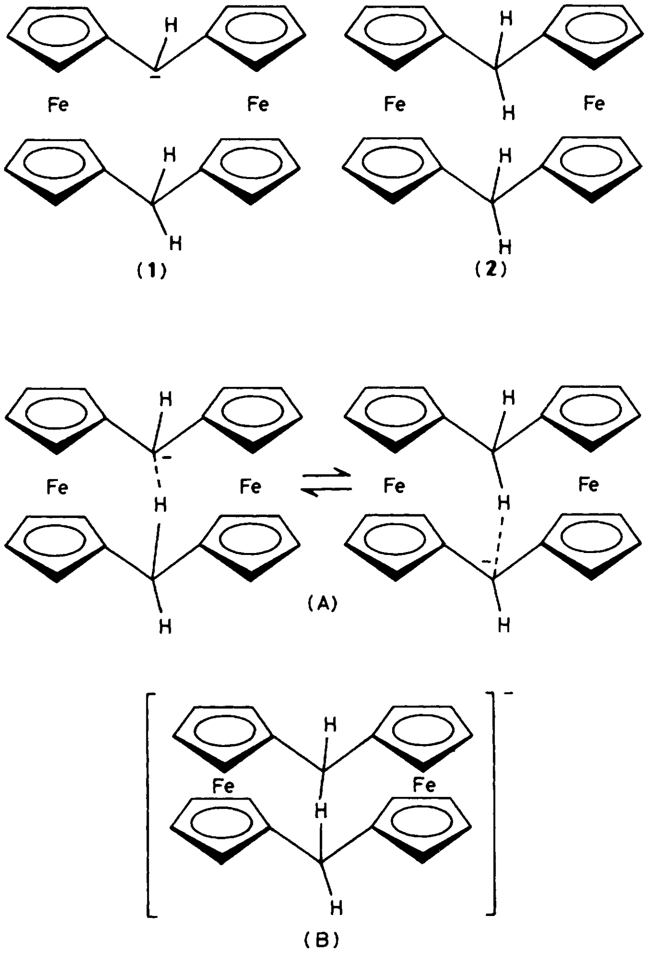
The temperature dependence of the ^{1}H n.m.r. spectrum of the carbanion of [1.1]ferrocenophane in tetrahydrofuran shows that a double-well potential rather than a single-well one governs the motion of the proton in the C–H–C bond.

Recently Mueller-Westerhoff *et al.* reported the first evidence for the existence of an intramolecular C–H–C hydrogen bond in the carbanion (**1**) prepared from [1.1]ferrocenophane (**2**) and butyl-lithium in [$^2H_8$]tetrahydrofuran (THF).[1] The appearance of one of the protons as a triplet at δ 4.51 in the ^{1}H n.m.r. spectrum of (**1**) about 1 p.p.m. downfield of the signal from the bridge protons in (**2**) was taken as evidence for the participation of this proton in a C–H–C hydrogen bond. Their n.m.r. spectrum remained unchanged in the entire temperature range from +30 to −70 °C. This was consistent with either rapidly equilibrating asymmetrically hydrogen bonded carbanions as in (A) of Scheme 1 or the presence of a symmetrically hydrogen bonded species as in (B). Thus their results did not allow insight into whether a single-well potential or a



Scheme 1

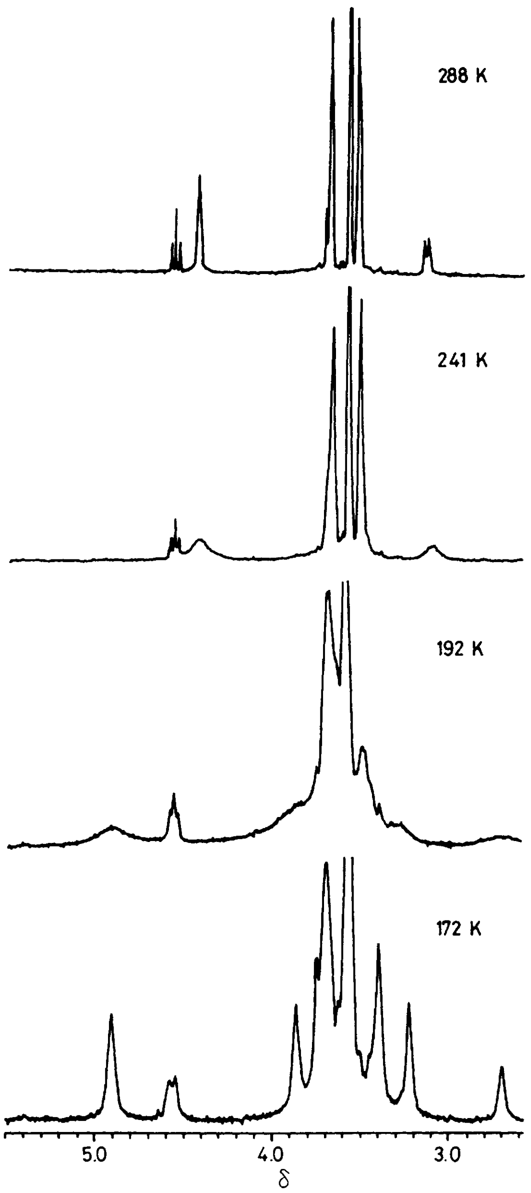


Figure 1. ^{1}H N.m.r. spectra of the lithium salt of the carbanion of [1.1]ferrocenophane (**1**) in $[^2H_8]$tetrahydrofuran at different temperatures. δ for the protons at the 2- and 5-positions of THF is set to 3.58.

double-well one is controlling the motion of the proton in the proposed hydrogen bond.

As part of our studies of structure and dynamics of hydrogen bonded carbanions[2] we have now reinvestigated the title system in the temperature interval +45 to −100 °C by ^{1}H n.m.r. spectroscopy. Contrary to the previous report the ^{1}H n.m.r. spectrum showed considerable temperature dependence (Figure 1). The spectrum at +20 °C was similar to that reported by Mueller-Westerhoff *et al.*[1] However, the ferrocene ring proton signal at δ 4.42 (4H) was found to broaden upon lowering the temperature. At −70 °C it had essentially disappeared and at −78 °C two new signals at δ 3.88 (2H) and 4.92 (2H) were observed. Similarly the doublet at δ 3.12 from the two *exo*-hydrogens was split into two new signals spaced at ±0.42 p.p.m. relative to the original signal. The one at higher field, *i.e.* at δ 3.54, was hidden under the ferrocene ring proton signal at δ 3.53. Also the spectrum of the other ferrocenophane protons showed considerable temperature dependence. At about −100 °C the *endo*-proton triplet at δ 4.56 had changed into a 1:1 doublet with a splitting approximately twice the triplet splitting measured in the fast exchange-averaged spectra. This is interpreted as due to coupling to one of the two non-equivalent *exo*-protons, *i.e.* the one attached to the methylene carbon. The coupling with the other *exo*-proton appears to be negligibly small.

All these observations appear to be consistent with an asymmetrically hydrogen bonded carbanion undergoing degenerate rearrangement as in (A) of Scheme 1. Thus our results exclude the possibility that the carbanion has a structure with a symmetrical hydrogen bond as in (B) of Scheme 1. The rate constant for the degenerate rearrangement was estimated to be 8×10^3 s^{-1} at −24 °C which corresponds to $\Delta G^\ddagger = 42$ kJ/mol.

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