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Preliminary Communication

One-bond CC and two-bond CH coupling constants in vinyllithium

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Abstract

A value of 35.9 Hz has been determined for the one-bond CC spin–spin coupling constant of vinyllithium at a natural abundance of ^{13}C. This is the lowest ^1J(CC) value so far observed for a monosubstituted ethene. The result is interpreted in terms of the s-electron distribution in the molecule.

Numerous papers devoted to structural analysis of organolithium compounds have appeared, and in many of them relevant NMR data have also been reported [1–7]. However, only a few one-bond CC spin–spin coupling constants have been determined for such compounds [8–11]. A ^1J(CC) coupling constant 56.8 Hz was found for triethylsilylethynyllithium [11] and one of 37 Hz for *trans*-1,2-dichlorovinyllithium [10]. Very recently ^1J(CC) couplings have been reported for phenyllithium [12,13]; for this compound a C_{IPSO}–C_{ORTHO} coupling constant of 27.8 Hz was found in tetrahydrofuran solution [12] and one of 29.5 Hz in diethyl ether solution [13], which is the smallest ^1J(CC) coupling constant observed for a benzene derivative.

Vinyllithium is an important reagent for organic synthesis, and its structure has been a subject of much interest. The NMR data published for this compound include the ^{1}H [14] and ^{13}C [15,16] chemical shifts and the geminal and vicinal ^{1}H–^{1}H [14,15] and the one-bond ^{13}C–^{1}H coupling constants [16]. In addition the ^{13}C–^{6}Li couplings constants have been determined at low temperature for various aggregates of the compound [15].

A knowledge of the value of ^1J(CC) in $H_2C{=}CHLi$, not available up to now, is of particular interest because it could shed some light on the s-electron distribution within the C=C and C–Li bonds in the molecule.

In all known cases, the value of ^1J(CC) for substituted ethenes is larger by *ca.* 10 Hz than the C_{IPSO}–C_{ORTHO} coupling in analogously-substituted benzene [17,18]. From this, it could be estimated that the ^1J(CC) value in vinyllithium should be about 39 Hz. The ^{13}C NMR spectrum of vinyllithium (saturated solution in Et_2O with some C_6D_6 present as lock) consists of two signals, at 134.63 ppm ($\delta(CH_2)$) and 182.76 ppm (δ(CLi)). The positions of the signals provide evidence that the tetrameric aggregate predominates under the conditions used (values of 132.69 ppm and 183.0 ppm were reported by Bauer *et al.* for this form of vinyllithium [15]). The signals are fairly narrow (see Table 1), and this indicates that the exchange processes in the aggregates are fast on the NMR time-scale. Dilution with more ether does not significantly influence the positions of the signals or their halfwidths, but a marked change takes place upon addition of TMEDA. Firstly both signals become considerably broadened (see Table 1) and secondly the signal assigned to the CHLi carbon is moved considerably towards lower field (δ(CHLi) = 192.40 ppm) and that from the CH_2 carbon moves to higher field by *ca.* 4 ppm ($\delta(CH_2)$ = 130.94 ppm). These chemical shifts indicate the presence of the dimeric form of vinyllithium; a value of $\delta(^{13}CLi)$ of 190.81 ppm and one of $\delta(^{13}CH_2)$ of 128.86 ppm were reported for the dimer at −90°C [15]. In the sample containing HMPA both forms are present in comparable amounts since the positions of the signals are between those found for the tetramer and the dimer (185.14 ppm and 133.09 ppm), and both signals are quite broad (39.0 Hz and 25.0 Hz, respectively).

The large widths of the signals in the samples containing HMPA and TMEDA made the measurements of ^1J(CC) rather difficult, and in fact a ^{13}C INADEQUATE NMR spectrum could be recorded only for solutions in pure ether (Fig. 1). The ^1J(CC) coupling of 35.8 Hz found from these spectra is almost halved compared with that for unsubstituted ethene (67.8 Hz [18]). Since the magnitude of ^1J(CC) couplings strongly depends on the s-character of the orbitals forming the C=C bond [3,17,18], the result indicates that the density of s-electrons within the C–C bond decreases markedly upon replacement of hydrogen by lithium. The decrease in the CC coupling constant is accompanied with an equally strong decrease in the one-bond CH coupling in the CHLi moiety. A value of ^1J(C1H1) of

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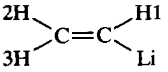
TABLE 1. Chemical shift ($\delta(^{13}C)$, ppm) and coupling constant (J, Hz) data for vinyllithium; all chemical shifts are reported against TMS; the data include also halfwidths of the bands ($\Delta S/2$) given in Hz.



Solvent	δ(C1)	ΔS1/2	δ(C2)	ΔS2/2	^1J(CC)	^1J(C1H1)
Et_2O [a]	182.76	3.1	134.63	4.3	35.8	93.5
Et_2O [b]	182.56	1.6	135.13	3.0	35.9	
Et_2O + HMPA	185.14	39.0	133.09	25.0	c.n.m. [c]	
Et_2O + TMEDA	192.40	19.8	130.94	11.2	c.n.m. [c]	93.3
THF	183.4 [d]		132.5 [d]			88 [d]
THF	183.00 [e]		132.69 [e]			
THF	190.81 [f]		128.86 [f]			

Solvent	^1J(C2H2)	^1J(C2H3)	^2J(C1H2)	^2J(C1H3)	^2J(C2H1)
Et_2O	145.1 [g]	146.7 [g]	13.6	6.3	11.8
Et_2O + TMEDA	ca. 146	ca. 146	c.n.m. [c]	c.n.m. [c]	c.n.m. [c]
THF	145 [d,g]	149 [d,g]			

[a] Saturated solution. [b] 3 M solution. [c] c.n.m. = could not be measured due to broadness of the signals. [d] Taken from ref. [16]. [e] Tetramer, 2 M solution, the spectrum measured at −90°C [15]. [f] Dimer, the spectrum measured at −90°C; taken from ref. [15]. [g] Can be interchanged.

93.5 Hz was found for vinyllithium ([16], 88 Hz), compared with the value for unsubstituted ethene of 159 Hz [3].

It is noteworthy that only in the case of $(Et_3Sn)_2C{=}CEt(BEt_2)$ is the value of ^1J(CC), namely 30.6 Hz, smaller than that in vinyllithium [19]; the former compound bears three strongly electropositive substituents at the double bond. In contrast the largest observed ^1J(CC) value, 172 Hz, is that for trifluorochloroethene [20]. Thus at present the total range covered by one-bond spin–spin couplings across the CC double bond is 141.4 Hz. This result clearly indicates that the parameter under discussion is a sensitive measure of the electronic structure of the C=C bond. It also confirms that the electronegativity of substituents has an important influence on the magnitude of the CC coupling. However, the rules that govern this influence are by no means simple. Comparison of the ^1J(CC) data for the

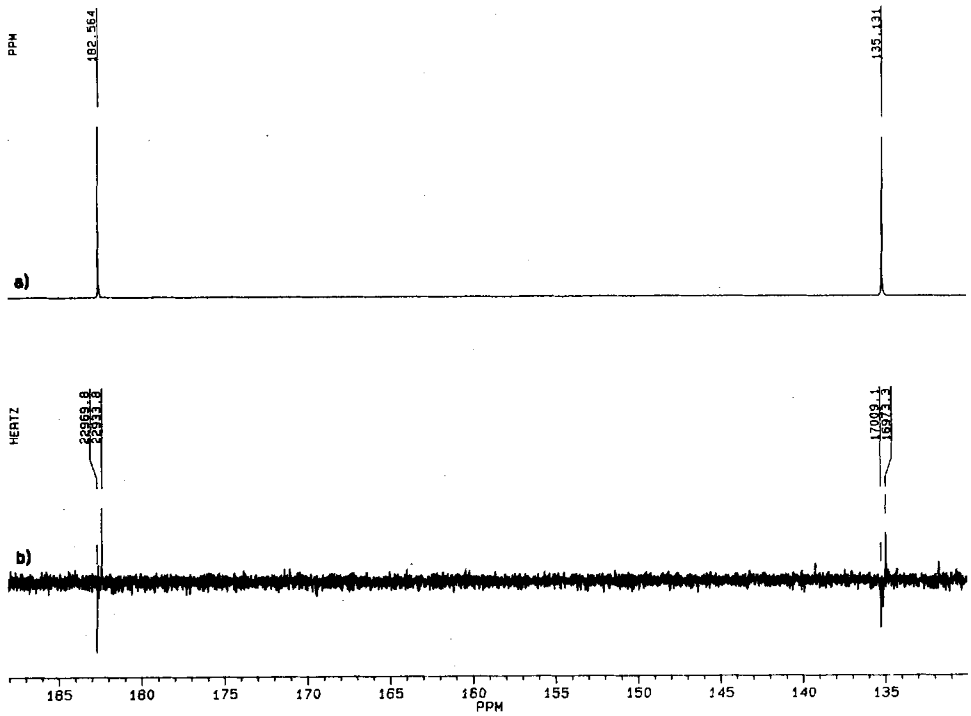


Fig. 1. ^{13}C {H} (a) and ^{13}C {H} INADEQUATE (b) spectra of vinyllithium recorded in Et_2O; 3 M solution.

compounds $H_2C{=}CHLi$, $ClCH{=}CClLi$, $H_2C{=}CH_2$ and *trans*-$ClCH{=}CHCl$, namely 35.6 Hz (this work), 37 Hz [10], 67.8 Hz[3] and 91.8 Hz [17], respectively, clearly shows that a simple additive scheme [18] does not apply in this case, since if it did a value of $^1J(CC)$ of *ca.* 61 Hz should be found for *trans*-$ClCH{=}CClLi$. Also the value predicted by the multiplicative scheme [20], *ca.* 56 Hz, though somewhat lower, is still too high. Further theoretical studies are required in order to provide full understanding of the experimental results.

In order to complete the set of spin–spin couplings for $CH_2{=}CHLi$ we also determined the absolute values of the relevant two-bond C–H couplings, which to the best of our knowledge have not previously been determined. The values are presented in Table 1 along with all the remaining ^{13}C NMR data.

Experimental details

All experiments were carried out under an inert argon atmosphere and the solvents were carefully dried. Vinyllithium was prepared as described previously [2]; it was dissolved in diethyl ether and to two samples was added TMEDA or HMPA. The ^1H NMR spectrum recorded in the Et_2O solution is in agreement with that reported for the tetramer; the data obtained for vinyllithium in Et_2O/TMEDA solution are slightly different, and resemble those reported for the dimer [15]. All spectra were recorded on a Bruker AM 500 spectrometer; a small amount of benzene-d_6 was present as lock. The INADEQUATE measurements were carried out using the standard Bruker microprogram (32-phase Freeman cycle with automatic data storage). The spectra were recorded in both proton-decoupled and proton-coupled modes; the $^2J(CH)$ values were assigned by selective proton decoupling. Typical conditions for standard proton-decoupled ^{13}C spectra were: acquisition 1.70 s, 0.6 Hz per point and 800 transients. The ^{13}C INADEQUATE spectra were recorded for $J = 50$ Hz; acquisition 1.7 s, pulse interval 2 s, 12h. The ^1H and ^{13}C chemical shifts were determined relative to internal C_6D_6 and recalculated relative to TMS.

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