X-Ray Crystal Structure of a Vinyllithium–Tetrahydrofuran Solvate (C₂H₃Li–thf)₄. Quantitative Estimation of Li–H Distances by ⁶Li–¹H HOESY
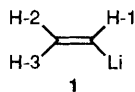
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Vinyllithium crystallizes with one equivalent of tetrahydrofuran (thf) and is tetrameric in the solid state whereas in thf solution a tetramer–dimer equilibrium (8 : 1, 2.0 mol dm⁻³, −90 °C) is present; lithium–hydrogen distances in solution are derived quantitatively by ⁶Li–¹H HOESY with *ca.* 0.2 Å accuracy.

One of the most simple and synthetically important organo-lithium compounds, vinyllithium **1**, has been found by NMR spectroscopy to be tetrameric in diethyl ether solution at low temperatures.[1] Likewise, a tetrameric structure for **1** was deduced from molecular weight determinations in tetrahydro-furan (thf) at +25 °C.[2] To our knowledge, no X-ray structure of **1** has been reported as yet.

Crystals of vinyllithium were grown from thf solutions of **1** and subjected to X-ray analysis.† The unit cell is tetragonal

$$
\begin{array}{c}
\text{H-2} \quad\quad \text{H-1} \\
\diagdown\!\!\diagup \\
\text{H-3} \quad\quad \text{Li} \\
\mathbf{1}
\end{array}
$$

(space group *P*4₂/*n*) and contains eight monomeric units. Four monomers are aggregated to form a cube-shaped tetramer (Fig. 1). Each lithium atom in the distorted cube is peripher-ally solvated by one thf ligand (omitted in Fig. 1). An *S*₄ axis extends vertically through the cube with respect to the orientation shown in Fig. 1. Similar cubic tetramers have been found for numerous other organolithium compounds.[3]
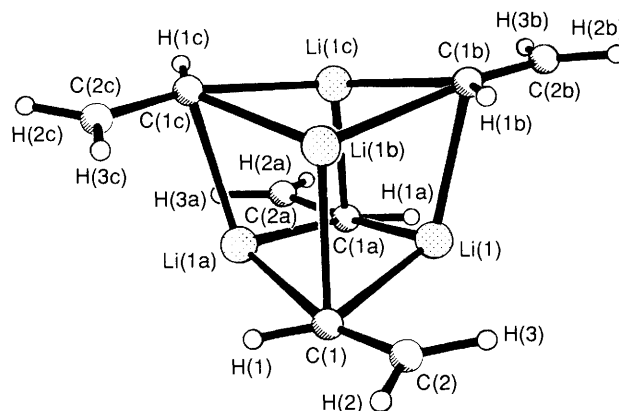
Fig. 1 Molecular structure of vinyllithium–thf, (C₂H₃Li·C₄H₈O)₄; thf ligands have been omitted for clarity. Selected bond distances (Å) and angles (°) are: C(2)–C(1) 1.406(30), C(1)–Li(1) 2.258(29), C(1)–Li(1a) 2.238(37), C(1)–Li(1b) 2.257(38), Li(1)–O(1) 1.967(39), C(1)–C(2)–Li(1) 52.1(12), C(1)–C(2)–Li(1a) 8.7(11), Li(1)–C(2)–Li(1a) 45.5(12), C(1)–C(2)–Li(1b) 52.6(13), Li(1)–C(2)–Li(1b) 54.8(14), C(2)–C(1)–Li(1) 98.4(16), C(2)–C(1)–Li(1a) 165.8(18), Li(1)–C(1)–Li(1a) 70.5(16), C(2)–C(1)–Li(1b) 97.7(16), C(2)–Li(1)–C(1) 29.5(8), C(1)–Li(1)–O(1) 114.6(15), C(1)–Li(1)–C(2a) 103.5(14).

For the NMR studies, compound 1 isotopically labelled with ^{6}Li (spin $I = 1$) was employed. At -90 °C, ^{1}H and ^{13}C NMR spectra indicate the presence of two species of 1 in [^{2}H$_8$]thf. From the multiplicities due to resolved ^{13}C–^{6}Li scalar coupling[4] these must be a tetramer and a dimer in ca. 8:1 molar ratio (2.0 mol dm^{-3}).‡ Dynamic processes are observed within the tetramer:[5] at -90 °C, a seven-line multiplet is present for the ^{13}C NMR signal of C-1, consistent with a static aggregate (coupling of ^{13}C with its nearest ^{6}Li neighbours; $J = 5.9$ Hz). Scrambling of the multiplet occurs upon warming. At -60 °C, a well resolved nine-line multiplet is detected, indicating the presence of a fluxional tetramer (time-averaged coupling of ^{13}C with all four ^{6}Li nuclei; $J = 4.4$ Hz). The NMR signal of C-1 of the dimer at -90 °C is a quintet ($J = 8.3$ Hz). The ^{13}C–^{6}Li coupling constants follow the '$J(^{13}$C–^{6}Li) $= 17/n$ Hz' rule.[6] At $+25$ °C, the ^{1}H and ^{13}C NMR chemical shifts of 1 in [^{2}H$_8$]thf are identical with those of the tetramer observed at -90 °C.

Short Li–H distances in organolithium compounds may be detected by ^{6}Li–^{1}H heteronuclear Overhauser effect spectroscopy (HOESY).[7] Fig. 2 shows the ^{6}Li–^{1}H HOESY spectrum of 1 in [^{2}H$_8$]thf. The order of the cross-peak intensities is: H-1 > H-3 > H-2.

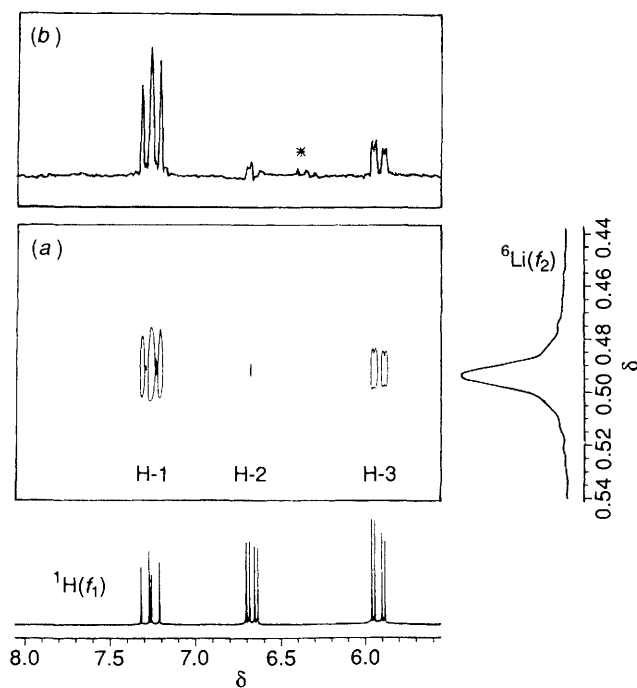As in the determination of homonuclear ^{1}H–^{1}H distances by 2D NOESY,[8] internuclear ^{6}Li–^{1}H distances may be derived from ^{6}Li–^{1}H HOESY spectra. The initial build-up rates, f, of the transient heteronuclear NOEs are related to the corresponding distances, r, by eqn. (1). Here, H^A denotes a proton whose distance from the lithium nucleus is known (e.g., from X-ray data), whereas H^X is a proton of unknown lithium separation.

$$[f(^6\text{Li–H}^A)/f(^6\text{Li–H}^X)]^{1/6} = r(^6\text{Li–H}^X)/r(^6\text{Li–H}^A) \quad (1)$$

Fig. 3(a) shows the dependence of the cross peak intensities in the ^{6}Li–^{1}H HOESY spectrum of 1 on the mixing time. Owing to the long spin–lattice relaxation time of ^{6}Li under the conditions of Fig. 3 [$T_1(^6\text{Li}) = 81$ s] the heteronuclear NOE
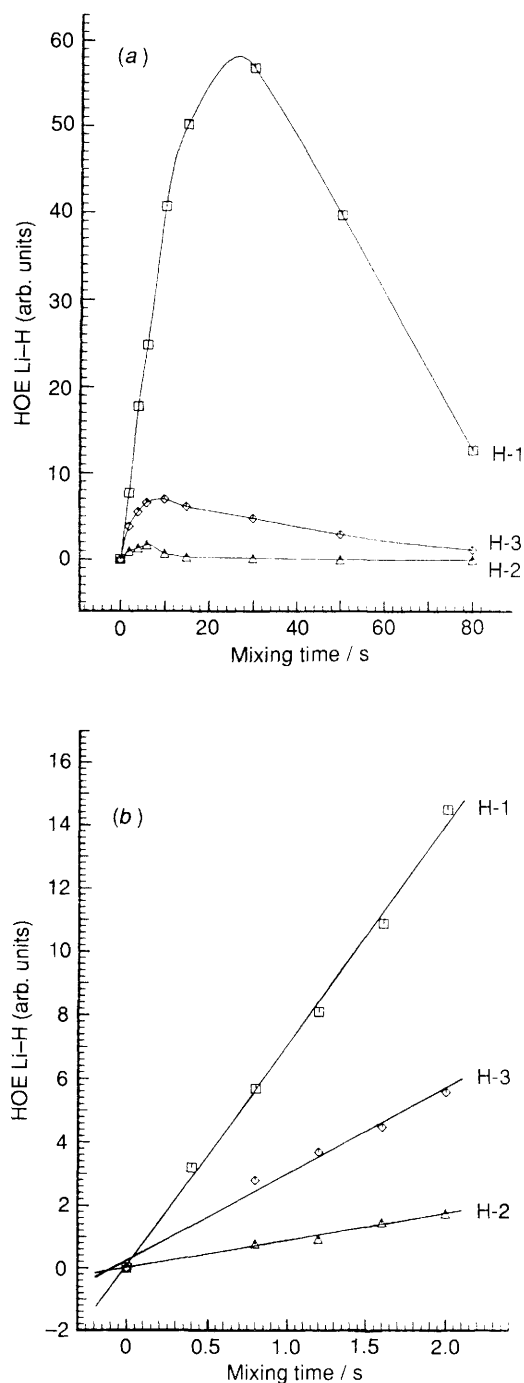

Fig. 2 Two-dimensional phase-sensitive ^{6}Li–^{1}H HOESY spectrum of vinyllithium 1 in [^{2}H$_8$]thf ($+26$ °C, $c = 2.0$ mol dm^{-3}, 9.4 T, $\tau_m = 2.0$ s);§ (a) contour plot; (b) f_1 cross section at $\delta_{Li} = 0.49$ ppm. The f_2 scale is expanded by a factor of 42. * = insufficiently suppressed quad image signal.

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‡ NMR data of 1 in [^{2}H$_8$]thf, -90 °C, 2.0 mol dm^{-3}: Tetramer: ^{1}H, δ 7.29 (dd, J 23.8 and 19.0 Hz, H-1), 6.65 (dd, J 19.0 and 7.4 Hz, H-2) and 5.91 (dd, J 23.8 and 7.4 Hz, H-3); ^{13}C, δ 183.00 (C-1) and 132.69 (C-2). Dimer: ^{1}H, δ 7.29 (dd, J 23.9 and 18.6 Hz, H-1), 6.50 (dd, J 18.6 and 8.8 Hz, H-2) and 5.66 (dd, J 23.9 and 8.8 Hz, H-3); ^{13}C, δ 190.81 (C-1) and 128.86 (C-2).

§ Further experimental NMR parameters were: 1024 t_2 data points (zero filled to 2048 points), f_2 spectral width 250 Hz, 128 t_1 increments (zero filled to 512 data points), f_1 spectral width 1000 Hz, 16 scans per t_1 increment, relaxation delay 3.1 s, 7 h spectrometer time, 90° pulse widths, 27 μs (^{6}Li) and 28 μs (^{1}H), 10 mm multinuclear probehead, 5 mm sample tube.

Fig. 3 (a) Dependence of the ^{6}Li–^{1}H HOE build-up in the tetrameric aggregate of 1 on the mixing time, τ_m ([^{2}H$_8$]thf, $+26$ °C, c 2.0 mol dm^{-3}). (b) Initial ^{6}Li–^{1}H HOE build-up in the tetrameric aggregate of 1, determined from cross-peak volume integrals for short mixing times. As compared to Fig. 2, lower digital resolution in both dimensions was employed to generate the individual 2D spectra.

Table 1 Intramolecular Li–H distances (Å) in the tetrameric aggregate of vinyllithium **1**[a]

	Li–H-1	Li–H-2	Li–H-3
Li–H-1	2.49	3.52	2.91
Li–H-2	2.73	3.86	3.19
Li–H-3	2.68	3.80	3.14

[a] Underlined values are weighted data ($<r^{-6}>^{-1/6}$) from the X-ray analysis (Fig. 1). Other data in horizontal rows represent distances derived from ^{6}Li–^{1}H HOESY by using the underlined reference distance of the same row. The mean overall deviation within the vertical columns is 0.2 Å.

(HOE) builds up much more slowly than is usually found in ^{1}H–^{1}H NOESY.

The initial HOE build-up rates may be derived from HOESY spectra with short mixing times [Fig. 3(b)]. The ratio of the slopes H-1 : H-2 : H-3 is 7.96 : 1.00 : 3.12. By using eqn. (1) the Li–H distance ratios involved may be derived: $r_{Li,H-1}/r_{Li,H-2} = 1.41$; $r_{Li,H-1}/r_{Li,H-3} = 1.17$; $r_{Li,H-2}/r_{Li,H-3} = 0.83$. By choosing a particular Li–H distance from the X-ray analysis of **1** (Fig. 1) as a reference, the remaining Li–H separations may be calculated. In matrix representation, Table 1 shows the ($<r^{-6}>^{-1/6}$) weighted internuclear Li–H distances from the X-ray analysis of **1** (underlined values) as well as the Li–H distances calculated from the HOESY data.

There is good agreement between the X-ray structural distances and the ^{6}Li–^{1}H HOESY data. The mean deviation within all columns of Table 1 is 0.2 Å. Thus, internuclear Li–H distances may be determined by using ^{6}Li–^{1}H HOESY with a reasonable accuracy. However, a suitable calibration distance must be given in this approach.

References

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