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Lithium atom exchange in solid *tert*-butyllithium

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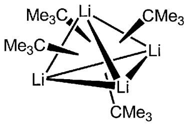
Lithium-7 NMR spectral lineshapes and T_1 measurements show that the lithium atoms in the solid tetrameric form of *tert*-butyllithium are rapidly exchanging between the apical sites of a tetrahedron with activation energies of 23.8 ± 0.2 and 23.0 ± 0.6 kJ mol^{-1}, above and below a phase transition (310 ± 3 K), respectively.

Inter- and intra-molecular exchange in organolithium oligomers in solution is well documented.[1] An example of intramolecular exchange is the scrambling of the *tert*-butyl groups within the lithium-6 labelled[Bu^{t}Li]$_4$ tetramer **1** in cyclopentane solution.[2]



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In this case the coupling $^1J(^{13}C^6Li)$ is observed between the α-carbon and all four ^{6}Li nuclei above 268 K. Below 251 K the exchange has stopped and coupling to only three ^{6}Li nuclei is observed. It has been shown that solid *tert*-butyllithium also exists as a tetramer.[3] These observations leads one to question whether a similar exchange process might occur in the solid state. Evidence for this comes from an early investigation of the ^{7}Li nuclear quadrupolar coupling constants (QCC) in solid methyllithium and ethyllithium where Lucken determined maximum values that were only a few kHz.[4] These values are unusually small and are much smaller than our calculated values for the [MeLi]$_4$ and [Bu^{t}Li]$_4$ tetramers.[5] Therefore it is expected that some kind of motional averaging might be responsible for the rather small QCC at ambient temperatures.

The ^{7}Li spectra of solid **1**, at various temperatures, are shown in Fig. 1.† At room temperature (293 K) we also observe a lineshape consistent with a ^{7}Li QCC of < 5 kHz. If an intramolecular exchange process is occurring, one should be able to observe changes in the spectral lineshapes as the temperature is reduced. This is indeed what happens between 200 and 150 K. Below 150 K the lineshape does not change and is consistent with a ^{7}Li QCC of 100 ± 3 kHz. The higher temperature lineshape shows that the quadrupolar interaction is nearly averaged to zero owing to either isotropic or pseudo-isotropic motion of the lithium atoms. Since the X-ray structure (at 180 K) shows lithium atoms occupying well defined sites located at the apices of a tetrahedron, pseudo-isotropic motion, *i.e.* exchange between tetrahedral sites, is the most likely averaging process. The lineshape changes indicate that the exchange rate is on the order of 10^5 s^{-1} in the temperature range 150–200 K, is $> 10^5$ s^{-1} above 200 K and $< 10^5$ s^{-1} below 150 K. In contrast the ^{1}H lineshape (not shown) changes very little in this temperature range. The relative temperature independence of the ^{1}H lineshape indicates that the *tert*-butyl groups are not exchanging, although rapid internal rotation of the methyl groups (about the C_α–C_β bonds) and the *tert*-butyl groups is expected to average the linewidth at these temperatures.

Another method for following molecular dynamics by NMR spectroscopy is through measurement of the spin–lattice relaxation time T_1. Fig. 2 shows a plot of the ^{7}Li T_1 as a function of temperature. It is quite clear that there is a well defined break in the T_1 curve at *ca.* 310 ± 3 K. We attribute this to a solid–solid phase transition. Above and below the phase transition temperature, the T_1 values are on the fast and slow motional side of the T_1 minimum, respectively. It would be informative to be able to discuss the lithium exchange process in terms of an exchange rate, *k*. This is possible if the spin–lattice relaxation rate can be described in terms of a single motional correlation time, τ_c, employing the commonly used BPP spectral density. Then the relaxation rate for a quadrupolar nucleus is given by eqn. (1)

$$R_1 = \frac{1}{T_1} = \frac{3\pi^2}{50}\frac{2I+3}{I^2(2I-1)}\chi^2\left[\frac{\tau_c}{1+(\omega_0\tau_c)^2}+\frac{4\tau_c}{1+(2\omega_0\tau_c)^2}\right] \quad (1)$$

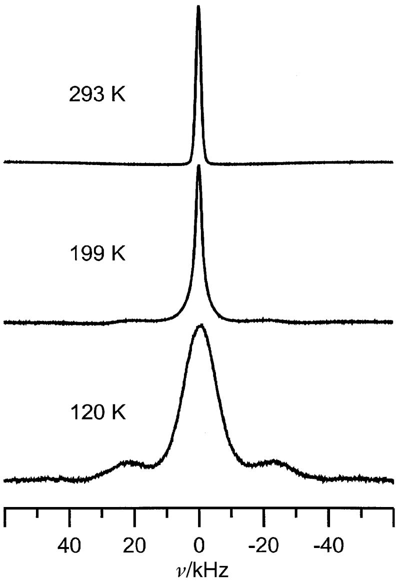

Fig. 1 The ^{7}Li spectra of solid *tert*-butyllithium at several temperatures.

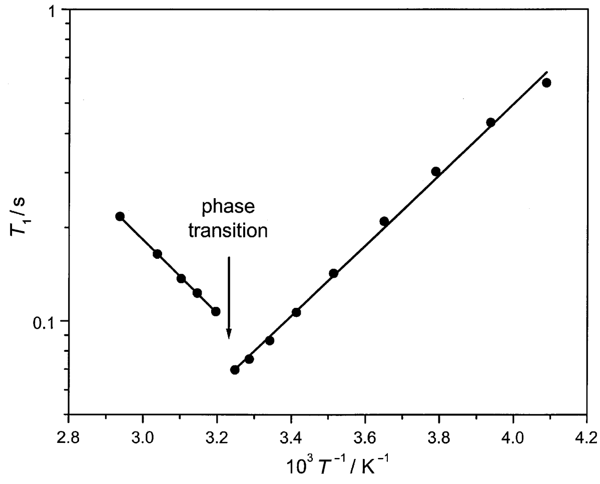

Fig. 2 Temperature dependence of the ^{7}Li T$_1$ for solid *tert*-butyllithium at a spectrometer frequency of 77.7 MHz.

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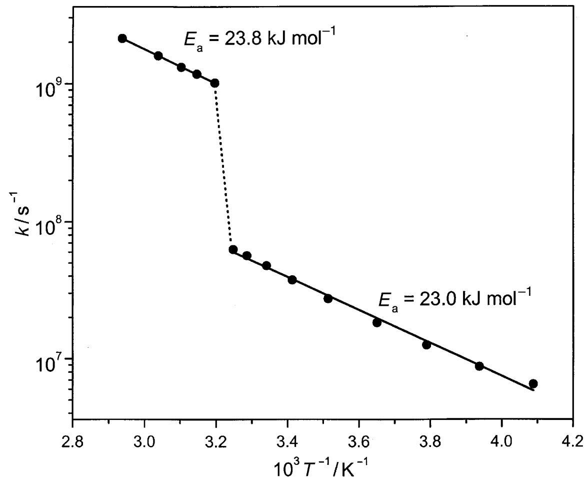

Fig. 3 Temperature dependence of the rate for lithium atom exchange in solid *tert*-butyllithium.

where I is the nuclear spin, χ is the nuclear QCC and ω_0 is the spectrometer (Larmor) frequency (in rad s^{-1}). If I, χ and ω_0 are known, τ_c values can be obtained from the T_1 measurements. The second assumption is that the lithium atoms are undergoing a 4-site exchange between equivalent tetrahedral sites. In that case the exchange rate is given as $k = 1/4\tau_c$.

Fig. 3 shows the temperature dependence of the lithium atom exchange rate. At the phase transition the rate changes by a factor of 16. The activation parameters for the exchange process are $E_a = 23.8 \pm 0.1$ kJ mol^{-1} and $k_\infty = 9.58 \pm 0.05 \times 10^{12}$ s^{-1} for the high temperature phase and $E_a = 23.0 \pm 0.6$ kJ mol^{-1} and $k_\infty = 4.85 \pm 0.33 \times 10^{11}$ s^{-1} for the low temperature phase. This analysis indicates that at 25 °C the lithium atoms in solid *tert*-butyllithium are exchanging at a rate of 8.5×10^8 s^{-1}!

Phase transitions are usually accompanied by changes in crystal and/or molecular structure. It would be of interest to compare a crystallographic study above 310 K with the earlier work at 180 K.[3]

Our calculated value of the ^{7}Li QCC for tetrameric **1** is 150 kHz.‡ This is larger than the observed value but does not take into account that the X-ray structure gives unrealistically short C–H bond lengths. Intermolecular effects are also not taken into account in this calculation. Details of our calculations and measurements of Li QCC values and chemical shift anisotropies in organolithium compounds will be published elsewhere.[5]

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Notes and references

† Solid **1** was obtained by stripping the solvent from a 1.5 M pentane solution of *tert*-butyllithium (Aldrich) inside an inert atmosphere box under argon. About 1 g of the white powder was packed into a small airtight 10 mm o.d. container. A separate sample was prepared for magic angle spinning experiments (^{13}C, ^{6}Li and ^{7}Li) which showed that the solid sample was pure. In particular, the ^{6}Li MAS spectrum, which gave excellent signal-to-noise and a linewidth of only 0.09 ppm, showed a single small impurity peak (2.1% of total peak intensity). The non-spinning ^{7}Li spectra were obtained at a frequency of 77.7 MHz with a Bruker ASX-200 spectrometer using a single channel wideline probe. Single pulse experiments using 3 μs pulses and relaxation delays of 10 s were employed. Quadrupolar echo experiments at the lowest temperature were identical to the single pulse experiments. The T_1 experiments employed the inversion recovery pulse sequence, π–t_d–$\pi/2$ with 8 t_d values for each T_1 determination. The magnetization curves as a function of delay time showed mono-exponential decay.

‡ We performed a DFT calculation using the B3LYP functional and a 6-31G** basis set. We have found that this combination gives QCC values in good agreement with experiment. The crystal structure geometry of a single [Bu^{t}Li]$_4$ tetramer was used. Calculations were done with the Gaussian 98 software package.[6]

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