ratios of "olefinic" to bridgehead polarization (Figure 1, bottom). The observed differences are far outside of the experimental limits of reproducibility. These results are incompatible with two rapidly equilibrating cations but can be accommodated readily by two discrete species generated by competing pathways.

The polarization of **2** in these experiments also deserves comment. With acetophenone or chloranil as sensitizer, **2** shows enhanced absorption indicating that it is generated after diffusive separation of the ion pairs. In contrast, the reaction with anthraquinone produces **2** in emission suggesting that it is generated from geminate ion pairs. This change in reaction parameter requires either that the ring opening is accelerated or that the pair lifetime is increased in the anthraquinone reaction.

To our knowledge, hexamethyl(Dewar benzene) is the first system in which two discrete minima on the radical cation surface correspond to a single minimum on the ground-state surface. Further examples of this interesting situation are under study.

Registry No. 1, 7641-77-2; **1** radical cation, 85293-78-3; chloranil, 118-75-2.

Structure and Dynamic Behavior of a Chiral Alkyllithium Compound: ^{13}C and ^{6}Li NMR of *sec*-Butyllithium

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Primary organolithium compounds in hydrocarbon solvents form a variety of aggregates,[4-6] $n = 6-9$, whose distribution varys with the temperature and which undergo at equilibrium fast inversion[7,8] at carbon bonded to lithium, faster interaggregate carbon-lithium bond exchange, and ever faster intraaggregate carbon-lithium bond exchange that is still fast relative to the NMR time scale at -100 °C.[6,8]

We have utilized the existence of scalar coupling between ^{13}C and directly bonded ^{6}Li[9,10] to investigate the nature of the bridge-bonded structure of $(RLi)_n$ aggregates and from its averaging, using NMR line-shape analysis, the dynamics of C, Li bond exchange.[6] Lithium-6 is used because ^{7}Li quadrupole-induced relaxation is often fast enough at low temperature to average ^{13}C, ^{7}Li coupling as well as give broad ^{7}Li NMR lines.[6]

We have now applied these techniques to study a secondary lithium compound with a chiral center, *sec*-butyllithium.[10] Our results described below provide an unprecedented wealth of structural detail as well as significant insight into dynamic behavior.

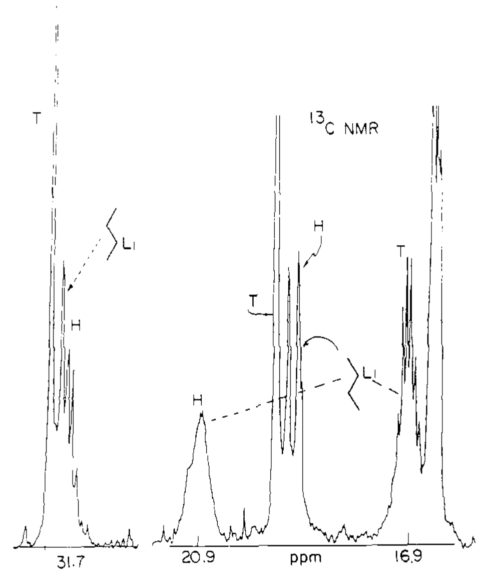

Figure 1. ^{13}C NMR of *sec*-butyllithium 2.0 M in cyclopentane at 232 K, 67.87 MHz.

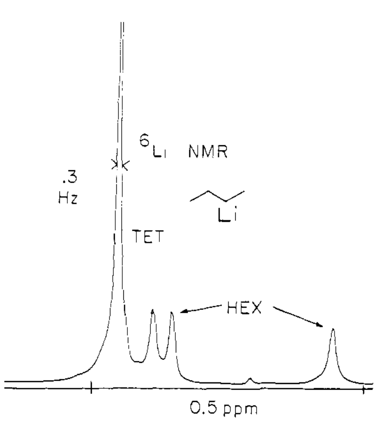

Figure 2. ^{6}Li NMR of *sec*-butyllithium 2.0 M in cyclopentane at 232 K, 38.73 MHz.

Table I. ^{13}C NMR of *sec*-Butyllithium 2 M in Cyclopentane at 220 K (ppm/Me_4Si)

	C_1	C_2	C_3	C_4
tet	19.27	16.89	31.69	15.98
hex	19.09	20.91	31.45	15.81
	28.85		31.31	
	18.75		31.22	
			31.11	

The ^{13}C NMR spectrum of a 2 M solution of *sec*-butyllithium[11,12] in cyclopentane at 232 K shows resonance for C_2 at 20.91 and 16.89 ppm, respectively (Figure 1). The latter is a septet, with relative intensities close to 1:3:6:7:6:3:1, and with splittings of 6.1 Hz, consistent with three lithiums coupled to each $^{13}C_2$, indicating the existence of nonfluxional or slowly fluxional tetramers; the 20.91 ppm absorption shows poorly resolved splitting of 3.25 Hz, reminiscent of propyllithium hexamer[6] in cyclopentane, with an overall line width consistent for fluxional hexamer.

With decreasing temperature the hexamer concentrates at the expense of tetramer, and from their respective C_2 peak areas, we derive ΔH and ΔS for the equilibrium

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[12] Using a Bruker WH-270 NMR spectrometer at 67.887 MHz, proton decoupling, 10-μs pulse, repeated every 2.048 s and with a Bruker WH-300 instrument.

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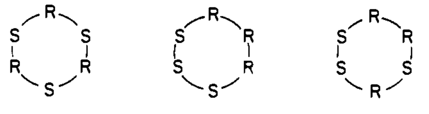
$$2R_6Li_6 \rightleftharpoons 3R_4Li_4 \qquad K_{258\ K} = 2.3\ M$$

to be 7 kcal and 28 eu, qualitatively consistent for dissocation.[13] Below 200 K the tetramer/hexamer ratio increases, accompanied by some precipitation, presumably hexamer.

Comparison of peak areas establishes the other shifts for tetramer and hexamer (Table I). The C_1, C_3, and C_4 resonances of hexamer show fine structure, e.g., *four* peaks for C_3 (Figure 1). We believe this arises from diasteromeric aggregates that invert slowly at C_2, relative to the NMR time scale. The latter effect was also observed for 2-lithiooctane and 4-*tert*-butylcyclohexyl)lithium.

Assuming that the *sec*-butyllithium hexamer exists as the octahedral structure[5] with the six alkyl groups arranged around the equatorial plane, there are 13 ways of arranging R_nS_{6-n} (n = 0–6), 10 being enantiomeric pairs, and three are R_3S_3 (**1**). But we



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observe only four resonances for C_3, which is just the number of molecular formulas of the diastereomers R_nS_{6-n} ($R_6 = S_6$, $R_5S = RS_5$, $R_2S_4 = R_4S_2$, R_3S_3). Then it appears that intraaggregate C, Li exchange must average the shifts among diastereomeric hexamers that have the same content but different structures, e.g., the three forms of R_3S_3, **1**, even at 173 K. This conclusion is supported by the ^{6}Li NMR, which consists, at 183 K, of five sharp lines $\Delta\nu \sim 0.3$ Hz, the large one correlating with tetramer and the others with hexamer (Figure 2).[14]

Above 232 K the fine structure of C_2Li of tetramer, due to $J(^{13}C, ^6Li)$ of 6.1 Hz, broadens out, fleetingly resolves into lines 4.6 Hz apart ($^3/_4$ of 6.1 Hz) aound 272 K and broadens again on further warming. We propose that a combination of *intra*- and *inter*aggregate carbon–lithium bond exchange, respectively, is responsible for these effects. By 272 K intraaggregate C, Li bond exchange becomes fast enough to give the spectrum of the fluxional tetramer. Above 272 K interaggregate exchange averages all ^{13}C, ^{6}Li couplings. By 300 K this effect averages the resonances of the diastereomeric hexamers with that for tetramer[15] to a single spectrum. Thus the order of decreasing rates of these dynamic processes is, for C, Li bond exchange, intraaggregate > interaggregate, both much faster than inversion at C_2Li. The intraaggregate exchange in the hexamers is so much faster than that for tetramer that the former is still fluxional (relative to the NMR time scale) at 173 K.

Finally at high concentrations, 6.7 M, the ^{13}C NMR of *sec*-butyllithium shows a weak six-line resonance, 1:3:5:5:3:1, at 10.52 ppm, separation 4.9 Hz. We propose that this comes from two overlaid 1:2:3:2:1 multiplets for diastereomeric dimers, whose centers are separated by 2.5 Hz.

In sum this work establishes *sec*-butyllithium to exist in hydrocarbon media as a mixture of dimer (minor), hexamer, and tetramer that undergoes at equilibrium fast intra- and interaggregate C, Li bond exchange and much slower inversion at C_2Li.

Acknowledgment. This research was supported by the National Science Foundation Grant 8007439. The NMR equipment at Ohio State University was financed in part by a grant from the National Science Foundation. We thank Dr. Charles Cottrell, Chemical Instrumentation Center, Ohio State University, for his help.

Registry No. *sec*-Butyllithium, 598-30-1.

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[13] Using IR, a Russian group obtained ΔH of 4.9 kcal: Serutun, V. M.; Antonov, N. G.; Zgonnik, V. N.; Kalninsh, K. K. *J. Organomet. Chem.*, **1978**, *145*, 265–267.

[14] 38.73-MHz, 15-μs pulse, repeated every 16.38 s, 500-Hz spectral width.

[15] The tetramer shows no shifts among diastereomers, since the alkyl groups are less crowded than in hexamers.

Solvation of the Methyl Radical and Its Implications

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In the absence of any specific chemistry, it is not immediately obvious how an alkyl radical in solution should be affected by a solvent—a dilemma that, among other consequences, seriously hinders attempts to determine radical conformation through ESR measurements.[1] As a first step in rectifying this situation, we wish to propose what we believe is the first quantitative treatment of a novel kind of solvation: solvation by *vibrational polarizability*.[2] This solvation mechanism should presumably be responsible for the vast majority of the solvent effects on radicals such as the methyl radical, but the mechanism may also have implications for a variety of other species.

Physically, the polarizability of a solute can lead to an interaction with the solvent because polarizability implies a fluctuating charge distribution and thus the creation of instantaneous dipoles. Accordingly, if the solvent is polar (or even merely polarizable) one gets dipole–induced dipole forces (or induced dipole–induced dipole—dispersion—forces).[3] This picture is, of course, rather schematic, but it is, nonetheless, the basis for the extremely useful Drude oscillator formulation of polarizability[3,4] in which the instantaneous dipole moment of a molecule, **m**, oscillates harmonically with a force constant equal to the reciprocal of the polarizability, α,

$$\mathcal{H} = \tfrac{1}{2}\alpha\omega^2\boldsymbol{\pi}^2 + (2\alpha)^{-1}\mathbf{m}^2 \qquad (1)$$

Here the Hamiltonian, $\mathcal{H}$, is expressed in terms of the frequency of oscillation, ω, and the momentum, $\boldsymbol{\pi}$, conjugate to **m**.

While the usual presumption in writing this equation is that the charge fluctuation is due to electrons continually redistributing themselves around fixed nuclei, there is no reason why one could not have a situation in which the oscillating dipole results from a vibration of a molecule which itself causes significant charge displacement. For example, a molecule that is symmetric (e.g., planar) in its equilibrium configuration and consequently does not have a permament dipole moment can instantaneously acquire one by vibrating into a less symmetric (e.g., bent) configuration.

The magnitude of the solvation free energy accruing from this *vibrational polarizability* is easily calculated from existing theory. If, as will often be the case, the dipole moment is proportional to the normal coordinate,[5] z,

$$m = \epsilon z \qquad (2)$$

where ϵ is a constant with units of charge, and if the vibration is harmonic, then eq 1 is still applicable with the (now) vibrational polarizability given in terms of the force constant k as

$$\alpha_v \equiv \epsilon^2/k \qquad (3)$$

By then applying the approach of Pratt and Hoye and Stell,[4] one can show that the classical molar solvation free energy of such

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