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VIBRATIONAL SPECTRA OF (t-C₄H₉⁶Li)₄ AND (t-C₄H₉⁷Li)₄: Raman Intensities and the Question of Li-Li Bonding

W. M. Scovell^a; B. Y. Kimura^b; T. G. Spiro^a

^a Department of Chemistry, Princeton University, Princeton, N.J., U.S.A. ^b Department of Chemistry, University of Illinois, Urbana, Illinois, U.S.A.

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VIBRATIONAL SPECTRA OF $(t\text{-C}_4\text{H}_9^6\text{Li})_4$ AND $(t\text{-C}_4\text{H}_9^7\text{Li})_4$ Raman Intensities and the Question of Li-Li Bonding.^{1a}

W. M. SCOVELL,^{1b} B. Y. KIMURA^{1c} and T. G. SPIRO^{1b}

Department of Chemistry, Princeton University, Princeton, N.J. 08540, U.S.A., and the Department of Chemistry, University of Illinois, Urbana, Illinois 61801, U.S.A.

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Raman frequencies and intensities in methylcyclohexane solution and infrared frequencies in Nujol mull, have been obtained and assigned for the skeletal modes of $(t\text{-C}_4\text{H}_9^6\text{Li})_4$ and $(t\text{-C}_4\text{H}_9^7\text{Li})_4$. A normal coordinate analysis, neglecting hydrogen atoms, gave an overall frequency fit of 2% with a reasonable set of valence force constants. The calculated eigenvectors were used to transform the Raman intensities into bond polarizability derivatives. Because of coordinate mixing and the inherent sign ambiguity of molecular polarizability derivatives, there are eight sets of bond polarizability derivatives which are consistent with the measured intensities. Only one set, however, gives reasonable polarizability derivatives for CC stretching and CCC bending, and also shows the requisite invariance to isotope substitution. This set gives a low value for the Li-Li polarizability derivative, and application of the delta function potential equation suggests that the extent of Li-Li bonding is small, amounting to perhaps 5% of the total bonding electron density in the Li_4C_4 cage. This conclusion is consistent with the failure to observe Li-Li spin-spin coupling in $(t\text{-C}_4\text{H}_9\text{Li})_4$.

INTRODUCTION

The bonding in lithium alkyls has been a subject of speculation since the discovery of their polymeric nature.² Depending on the alkyl group, these compounds may be tetrameric or hexameric. Methyl-lithium is known³ to contain a regular tetrahedron of lithium atoms with triply bridging methyl groups above the faces of the tetrahedron. Ethyllithium is hexameric in hydrocarbon solutions,⁴ and a distorted octahedral arrangement of the lithiums has been suggested;² the crystal structure shows extended chains of interacting tetramers.⁵ *t*-Butyllithium, the subject of the present study, is tetrameric in solution,^{4,6} and spectroscopic evidence favors a regular tetrahedral structure.⁶

These oligomers are electron-deficient, in the sense that there are more interatomic contacts than there are valence electron pairs available for bond formation.⁷ Localized four-centered bonds, involving a triangle of lithium atoms and the bridging carbon atom of an alkyl ligand, are consistent with the polyhedral structures. Each such four-centered bond would contain one electron pair, giving a Li-C bond order of 1/3. Alternatively, there could be extensive electron delocalization in molecular orbitals extending over the entire alkyl lithium cage,³ and therefore a significant degree of Li-Li bonding. In fact, two independent molecular

orbital calculations yield Li-Li overlap populations comparable to those of Li-C.^{8,9} In favor of significant Li-Li bonding is the observation that the lithium clusters exhibit marked stability in mass spectral fragmentation patterns.^{10,12} Appearance potentials show that an alkyl group dissociates at energies well below those needed to start disrupting the lithium cage.^{10,11} On the other hand Brown *et al.*¹³ were unable to detect any ⁶Li-⁷Li nuclear spin coupling in either methyl- or *t*-butyllithium, and estimated that the coupling constant was less than 3% of what might reasonably be expected for a full Li₂ bond.

Recent studies¹⁴⁻¹⁷ suggest that Raman spectroscopy offers a sensitive technique for evaluating metal-metal interaction in bridged polynuclear complexes. It was with this application in mind that the present vibrational spectroscopic study of *t*-butyllithium was undertaken.

EXPERIMENTAL

Methyl cyclohexane solutions, 1.19 M in $(t\text{-Bu}^6\text{Li})_4$ and $(t\text{-Bu}^7\text{Li})_4$ were prepared and sealed in NMR tubes. The experimental details have been described elsewhere.¹²

Raman spectra were obtained *in situ* using transverse excitation by the 6471 Å line of an Ar⁺/Kr⁺

mixed gas laser (Coherent Radiation Model 52). The Raman spectrometer and its calibration have been described elsewhere.¹⁵ Depolarization ratios, ρ_p , were obtained by analyzing the scattered light with a polarized disk. Raman intensities (band areas) were measured with reference to the 847 cm^{-1} band of the methylcyclohexane solvent, which was in turn calibrated against the 459 cm^{-1} (ν_1) band of CCl_4 in a mixture of the two liquids. Overlapping bands were resolved with the aid of a DuPont 310 Curve Resolver.

After completion of the Raman measurements, the sample tubes were opened in an inert atmosphere, the solvent was evaporated, and the *t*-butyllithium residues were milled with Nujol and sealed in polyethylene infrared cells. Infrared spectra were kindly recorded by Miss B. Prescott, at Bell Telephone Laboratories, Murray Hill, N.J., using a Beckman IR-11 spectrophotometer.

SPECTRA AND ASSIGNMENTS

The vibrational frequencies observed in this study are essentially in agreement with those of Weiner *et al.*,⁶ although our data extend below 500 cm^{-1} . Above 1200 cm^{-1} the vibrations primarily involve hydrogen atom motions. These were discussed by Weiner *et al.*⁶ and are not considered in this study since most framework modes are expected below 1200 cm^{-1} . The Raman spectrum in this region for $(t\text{-Bu}^6\text{Li})_4$ is shown in Figure 1. Infrared and Raman frequencies are listed in Table I.

Weiner *et al.*⁶ inferred a tetrahedral structure for the *t*-butyllithium tetramer from the finding that a

TABLE I

Vibrational frequencies (cm^{-1}) below 1200 cm^{-1} for *t*-Butyllithium

$(t\text{-C}_4\text{H}_9^6\text{Li})_4$		$(t\text{-C}_4\text{H}_9^7\text{Li})_4$	
Raman ^a	Infrared ^b	Raman ^a	Infrared ^b
1133 p	1130	1133 p	1130
	990		990
928 dp	930	928 dp	930
c	780	c	780
597	d	568 dp	d
566 p		524 p	
	533 sh		522 sh
499 dp	496 s	486 dp	480 s
468 p		463 p	
427 dp	429 s	421 dp	415 s
385 dp	384 m	379 dp	385 m
	328 s		318 s
286 dp	291 s	288	290 s
191 p		191 p	
169 dp	169 m-w	166 dp	168 m-w
140 dp	142 m	140 dp	141 m
101 dp		101 dp	

Symbols: p = polarized, dp = depolarized, s = strong, m = medium, w = weak, sh = shoulder.

^a 1.19 M methylcyclohexane solution.

^b Bands above 600 cm^{-1} are from Weiner *et al.*⁶

^c Obscured by solvent band.

^d Obscured by 533 cm^{-1} envelope.

polarized Raman band at 563 cm^{-1} for ^6Li shifts to 521 cm^{-1} for ^7Li and does not appear in the infrared, observations which we confirm. This isotope shift is that expected for pure lithium motions and Weiner *et al.* assigned the mode to symmetric LiC stretching. If the molecular sym-

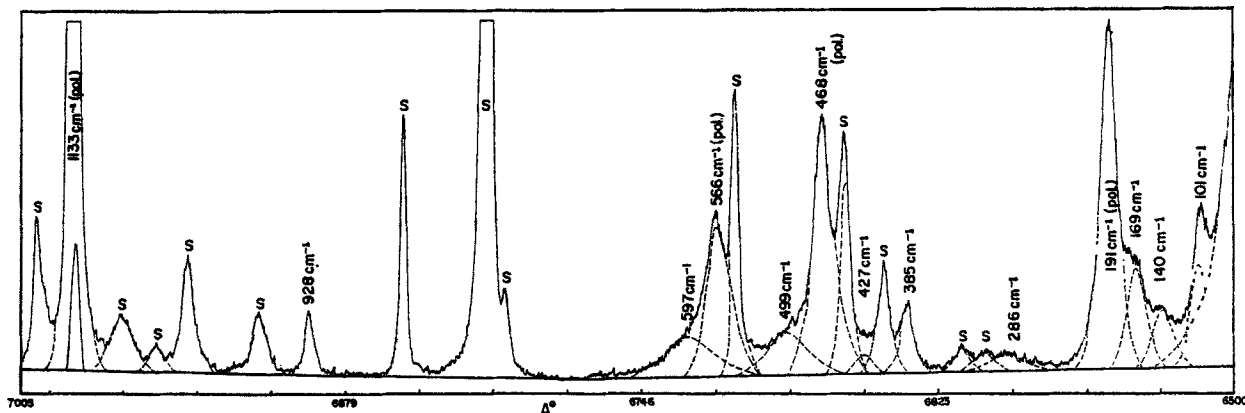


FIGURE 1 Raman spectrum of $(t\text{-C}_4\text{H}_9^6\text{Li})_4$ in methyl cyclohexane (1.19 M). Bands due to the solvent are denoted by S. Instrument conditions: 6471 \AA Kr^+ laser excitation; slit-width = 7 cm^{-1} ; sensitivity = 10^{-9} ; scan rate = $8\text{ \AA}/\text{min}$; time constant = 3 sec.

metry were lower than T_d (e.g. C_{4v} in a puckered 8-membered ring) this mode would be infrared active as well. Another test for cubic symmetry is provided by depolarization ratios, which must be zero for all totally symmetric modes. We find that the ratio is zero, within experimental error, for the 563 cm^{-1} (here observed at 566 cm^{-1}) band, as well as for a band at 191 cm^{-1} (not reported by Weiner *et al.*). Two other polarized bands, at 1133 and 468 cm^{-1} have non-zero ratios, but infrared coincidences and our normal coordinate calculations, presented below, indicate that non-totally symmetric modes are included in these band envelopes. Therefore we feel that the spectroscopic data are entirely consistent with a T_d structure for (*t*-BuLi)₄.

This structure is illustrated in Figure 2 and a set of internal coordinates for the framework is indicated. The T_d representations spanned by this set of coordinates is given in Table II. As always in

TABLE II

Contributions of internal coordinate types to the vibrationally active modes in $[\text{LiC}(\text{C}_3)]_4$

Internal coordinate	Number of contributions to each symmetry class		
	A	E	T ₂
D, (LiLi) bond	1	1	1
X, (LiC) bond	1	1	2
r, (CC) bond	1	1	2
γ , (CCC) angle	1	1	2
θ , (LiCC) angle	1	2	3
Total	5	6	10
Redundancies	1	1	2

polyhedral molecules there are cyclic redundancies among alternative internal coordinates. In the present case we could have used CLiC and LiCLi bending coordinates instead of the LiLi interaction. However, our intent was to evaluate LiLi bonding from Raman intensities and the LiLi coordinate provides the appropriate eigenvector elements for the analysis.

The four expected A_1 modes are observed. The one at 1133 cm^{-1} can be assigned primarily to CC stretching while the one at 468 cm^{-1} is at an appropriate frequency for CCC bending. The bands at 566 cm^{-1} and 191 cm^{-1} are therefore attributed to LiLi and LiC stretching, with these two coordinates highly mixed. The two modes to

which they are primary contributors are the in- and out-of-phase breathing modes of the central Li_4C_4 cluster. The isotope shift for the higher frequency (in-phase) mode indicates that the vibration primarily involves motion of the lighter lithium atoms, whereas the lower frequency vibration, which shows no isotope shift, evidently involves motion of the carbon atoms primarily.

In principle the E modes can be distinguished from the T_2 modes because the latter are active in the infrared whereas the former are not. In practice the distinction is blurred by accidental degeneracies, and by breakdown of the selection rules in the solid state infrared spectra. Assignments of these modes were made with the aid of the normal coordinate analysis.

NORMAL COORDINATE ANALYSIS

An approximate normal coordinate analysis was carried out to explore the main features of the skeletal force field and to obtain eigenvectors necessary for the analysis of the Raman intensities. Hydrogen atoms were omitted from the calculation and the methyl groups were given an effective mass of 15. The LiLi and LiC distances were assumed to be the average of those in ethyl- and methyl-lithium^{3,5} and standard CC distances and CCC angles were used for the *t*-butyl groups.¹⁸ These molecular parameters are given in Figure 2.

Schachtschneider's programs¹⁹ GMAT and FPRT were used for the construction of the

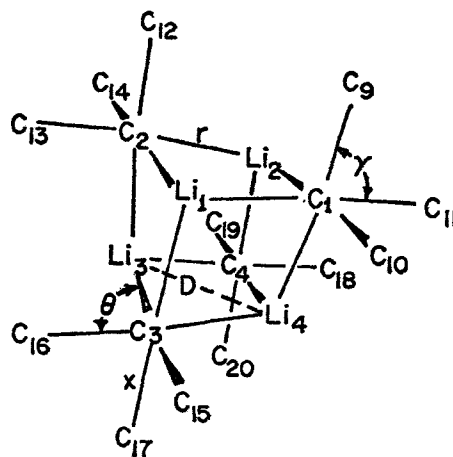


FIGURE 2 Structure of (*t*-C₄H₉Li)₄ (hydrogen atoms omitted) with internal coordinates defined. Molecular parameters are $r_{\text{LiC}} = 2.21\text{ \AA}$, $D_{\text{LiLi}} = 2.52\text{ \AA}$, $x_{\text{CC}} = 1.54\text{ \AA}$, $\gamma_{\text{CCC}} = 109^\circ 28'$.

G matrix and for solution of the secular equations, with least squares adjustment of the force constants. A valence force field was used to construct the F matrix. The matrices were factored using symmetry coordinates generated from the internal coordinates by standard group theoretical techniques. In all calculations the ^6Li and ^7Li isotope molecules were treated *simultaneously*. Four primary force constants were initially adjusted to calculate the four skeletal A_1 frequencies using the assignments discussed above. It was immediately apparent that the kinetic couplings were so large that the A_1 frequencies could not be satisfactorily reproduced without the use of interaction force constants. Accordingly LiLi, LiC stretch-stretch, and LiC, CCC stretch-bend interaction constants were introduced and adjusted to improve the A_1 fit. The E and T_2 frequencies were then calculated and matched with the observed spectral features. The fifth primary force constant, for LiCC bending, was adjusted to calculate two of the lowest frequencies, at 169 and 101 cm^{-1} (E and T_2). The seven force constants were then refined further and it was possible to calculate the 14 skeletal frequencies of each isotopic molecule to within an average deviation of 2.0%. The results are shown in Table III.

TABLE III

Normal coordinate analysis results

Symmetry Species	Frequencies (cm^{-1})			
	$(t\text{-C}_4\text{H}_9^6\text{Li})_4$		$(t\text{-C}_4\text{H}_9^7\text{Li})_4$	
	Observed ^a	Calc. ^b	Observed ^a	Calc. ^b
E	— ^c	1563	— ^c	1563
T_2	— ^c	1563	— ^c	1563
T_2	1133	1136	1133	1136
A_1	1133	1133	1133	1133
T_2	597	603	568	571
E	597	600	568	562
A_1	566	564	524	524
T_2	499	491	486	489
E	468	468	463	464
A_1	468	462	463	460
T_2	427	433	421	426
T_2	385	394	379	367
T_2	286	311	288	294
A_1	191	185	191	185
E	169	159	166	159
T_2	101	108	101	107
E	— ^d	41	— ^d	41

^a Raman (solution) frequency.

^b Overall frequency fit, 2.0%.

^c Region above 1200 cm^{-1} not explored (see text).

^d Unresolved from Raman exciting line wing.

A weak band at 140 cm^{-1} observed in both the Raman and the infrared spectra could not be calculated with any set of reasonable force constants. It may possibly arise from a torsional motion of the methyl group.²⁰ There are also extra infrared bands at 533 (522 for Li^7) and 328 (318 for Li^7) cm^{-1} which are probably components of the T_2 modes assigned at 499 and 286 cm^{-1} in the Raman spectrum, the splittings presumably arising from lowered symmetry in the solid state. All frequencies calculated below 1200 cm^{-1} correspond to observed spectral features, except that at 41 cm^{-1} (E) which lies below the exciting line cut-off in our Raman spectra.

TABLE IV

Valence adjusted/force constants ($\text{mdyne}/\text{\AA}$)

Primary Constants	
CC stretch	7.39
LiC stretch	0.77
LiLi stretch	0.27
CCC bend	0.55
LiCC bend	0.05
Interaction constants	
Li(1)C(1), Li(1)Li(2) stretch, stretch ^a	-0.04
LiC, CCC stretch, bend (adjacent)	-0.07
Li(1)C(1), Li(1)Li(3) stretch, stretch ^a	-0.0005

^a Numbers in parentheses refer to atom labels in Figure 2.

Asymmetric CC stretching modes (E and T_2) are predicted at 1563 cm^{-1} , in a region not explored in this study. Weiner *et al.*⁶ report Raman bands at 1474, 1436, 1385 and 1360 cm^{-1} . Any two of these could be calculated with the introduction of reasonable CC, CC stretch, stretch interaction constants. There is little point in doing so, however, since the calculation of the CC force constant is in any case unrealistic because of the neglect of CH deformation modes, which should mix substantially with the CC modes. (Inclusion of hydrogen atoms makes the G matrix prohibitively large.) Indeed the CC force constant needed to calculate the 1133 A_1 mode, 7.39 $\text{mdyn}/\text{\AA}$, is unreasonably high, and suggests interaction with an A_1 methyl rocking mode²¹ which should lie at lower frequency. However the intensity of the latter mode is sufficiently low that it escapes detection, so that the contribution of CC stretching to its eigenvector must be small (see next section).

The other force constants (Table IV) seem reasonable although there are no closely related systems for comparison. The LiC stretching con-

TABLE V
Potential energy distribution for (*t*-C₄H₉⁶Li)₄

Frequency	V _{CC} ^a	V _{LiC}	V _{LiLi}	V _{CCC}	V _{LiCC}	V _{LiC, LiLi}	V _{LiC, CCC}
1563 (E)	90.1	2.5	0	6.6	0.9	0	0
1563 (T ₂)	90.2	2.2	0	6.6	0.9	0	0
1136 (T ₂)	89.2	8.0	0	7.1	0.5	0	-4.9
1133 (A ₁)	90.5	6.2	0	7.1	0.5	0	-4.3
600 (E)	3.2	78.9	18.6	3.4	4.6	-10.1	0
603 (T ₂)	6.5	96.7	2.6	5.6	4.1	-1.3	-14.5
564 (A ₁)	0.7	38.5	91.3	1.2	6.2	-31.4	-4.3
491 (T ₂)	9.3	13.0	1.1	72.0	5.8	0	-0.9
468 (E)	5.8	3.0	2.9	85.3	3.7	-0.8	0
462 (A ₁)	8.5	25.8	4.2	79.7	5.1	5.5	-29.2
433 (T ₂)	4.4	5.0	3.9	80.6	12.1	0.5	-6.6
394 (T ₂)	0	19.2	71.4	9.4	3.2	-2.8	0
311 (T ₂)	0.3	46.3	21.1	16.3	8.2	3.2	4.4
185 (A ₁)	0.3	51.3	5.5	9.7	9.3	8.9	14.4
159 (E)	0.8	8.4	3.5	2.0	84.2	1.4	0
108 (T ₂)	0	10.1	0	0.1	89.7	0	0
41 (E)	0	8.3	60.4	0	26.1	5.9	0

^a V_{ij} is the normalized contribution to the potential energy from F-matrix elements of the type F_{ij} (V_{ii} is labelled V_i).

stant is quite low as would be expected for a triply bridging alkyl group. Even multiplying by three, to take into account that the maximum LiC bond order is 1/3, gives a value, 2.3 mdyne/Å, which still suggests a weak LiC bond. It happens that the LiLi stretching constant is the same as that found for gaseous Li₂, and indeed the LiLi distances are also very similar. However the redundancies inherent in (*t*-BuLi)₄ render the comparison invalid. The vibrational frequencies could have been calculated equally well using CLiC and LiCLi bending force constants instead of the LiLi force constant. It has been shown²² that this sort of ambiguity in the force field does not, however, materially affect the calculated eigenvectors.

The potential energy distribution for (*t*-Bu⁶Li)₄ (Table V) shows that the modes above 1000 cm⁻¹ can be characterized as essentially CC stretching. The four modes between 430 and 500 cm⁻¹ are predominantly CCC deformation and the two modes at 108 and 159 cm⁻¹ are mainly LiCC deformation (twisting modes of the *t*-butyl group). The remaining modes have heavy admixtures of LiC and LiLi stretching.

POLARIZABILITY DERIVATIVES

From the measured intensities and depolarization ratios of the A₁ Raman bands, Table VI, normal

TABLE VI
Intensity data for (*t*-C₄H₉Li)₄ molecules

(<i>t</i> -C ₄ H ₉ ⁶ Li) ₄ ν(cm ⁻¹)	ρ _p ^a	R ^b	$\bar{\alpha}'_Q$
1133	.26	1.00	1.820
566	.00	.23 ₆	.705
468	.06	.35 ₂	.756
191	.00	.37 ₂	.392
(<i>t</i> -C ₄ H ₉ ⁷ Li) ₄ ν(cm ⁻¹)	ρ _p	R	$\bar{\alpha}'_Q$
1133	.26	1.00	1.820
524	.00	.27 ₈	.727
463	.06	.29 ₈	.692
191	.00	.37 ₈	.394

^a ρ_p = depolarization ratio for polarized incident light and analyzed scattered light.

^b R = measured intensity relative to that of the 1133 cm⁻¹ band.

mode polarizability derivatives, $\bar{\alpha}'_Q$, were calculated in the usual manner.²³ These were then converted to internal coordinate polarizability derivatives, $\bar{\alpha}'_{u_i}$, via the transformation,²³

$$\bar{\alpha}'_{Q_i} = \sum_j N_j l_{ij} \bar{\alpha}'_{u_j} \quad (1)$$

where l_{ij} is the eigenvector element (Table VII) connecting the *i*th normal coordinate, Q_{*i*}, with the A₁ symmetry coordinate, S_{*j*}, made up from the *j*th

TABLE VII
A₁ Eigenvectors for (*t*-C₄H₉Li)₄

$\nu(\text{cm}^{-1})_{\text{calc.}}$	Q _i	<i>(t</i> -C ₄ H ₉ ⁶ Li) ₄			
		<i>l</i> _{LiC}	<i>l</i> _{LiLi}	<i>l</i> _{CC}	<i>l</i> _{CCC}
1133	Q ₁	.2461	.0176	-.3044	.2036
564	Q ₂	.3062	.8015	.0135	.0410
462	Q ₃	.2051	-.1403	.0380	.2775
185	Q ₄	-.1160	.0647	-.0026	.0388
<i>(t</i> -C ₄ H ₉ ⁷ Li) ₄					
1133	Q ₁	.2451	.0144	-0.3044	.2036
524	Q ₂	.3081	.7249	0.0166	.0688
460	Q ₃	.1782	-.2036	0.0366	.2720
185	Q ₄	-.1155	.0660	-0.0026	.0387

internal coordinate u_j and N_j is the number of internal coordinates in the set.

Since only the four skeletal A₁ intensities are under consideration, there are four simultaneous equations in the transformation.²⁴ Because of the

restricted nature of the normal coordinate analysis, contributions to Eq. (1) from CH coordinates were performed neglected. The contributing eigenvector elements for CH stretching should indeed be small, while for the CH deformation coordinates, the associated polarizability derivatives are expected to be close to zero. The approximate nature of the force field also introduces uncertainty in the calculated eigenvectors. An attempt was made to gauge this uncertainty by systematically varying the force constants by up to 10%, the overall frequency fit staying within 2–4%. Changes in the major eigenvector elements were always less than 10%, as were the resulting changes in the major internal coordinate polarizability derivatives.

Because Raman intensity is proportional to $(\bar{\alpha}'_Q)^2$, the signs of the $\bar{\alpha}'_Q$ are undetermined. Both signs must be considered for each $\bar{\alpha}'_Q$, and the four simultaneous equations therefore have sixteen possible sets of solutions, divided into eight pairs which differ only in sign. Fortunately there are criteria available which provide reasonable grounds

TABLE VIII
Sets of solutions to equation (1)

Sign Combination*	1 (--++)	2 (-+-)	3 (-+-)	4 (-+-)	5 (-+++)	6 (----)	7 (-+-)	8 (----)
$\bar{\alpha}'_{\text{CCC}}$								
⁶ Li	0.665	-0.858	-0.119	-0.076	0.672	-0.866	-0.112	-0.082
⁷ Li	0.605	-0.798	-0.183	-0.011	0.672	-0.868	-0.115	-0.079
Δ^b	0.060	0.060	0.067	0.065	0.000	0.002	0.003	0.003
$\bar{\alpha}'_{\text{CC}}$								
⁶ Li	1.830	1.285	2.042	1.072	2.050	1.071	2.260	0.857
⁷ Li	1.728	1.400	1.942	1.178	2.042	1.076	2.260	0.863
Δ	0.102	0.115	0.100	0.106	0.008	0.005	0.000	0.006
$\bar{\alpha}'_{\text{LiC}}$								
⁶ Li	-0.709	0.552	0.587	-0.744	-0.478	0.322	0.815	-0.973
⁷ Li	-0.763	0.605	0.538	-0.695	-0.482	0.325	0.819	-0.977
Δ	0.054	0.053	0.049	0.049	0.004	0.003	0.004	0.004
$\bar{\alpha}'_{\text{LiLi}}$								
⁶ Li	-0.093	0.126	-0.712	0.743	0.494	-0.462	-0.124	0.156
⁷ Li	-0.131	0.165	-0.758	0.792	0.495	-0.461	-0.133	0.166
Δ	0.038	0.039	0.046	0.049	0.001	0.001	0.009	0.010
$\Sigma(\Delta)^c =$	0.254	0.267	0.259	0.269	0.013	0.011	0.016	0.023
Ratios $\bar{\alpha}'_{\text{Q}_2} / \bar{\alpha}'_{\text{Q}_3}$	1.19	1.20	1.22	1.23	0.98	0.97	0.95	0.95
	0.92	1.04	0.93	0.93	1.09	1.07	1.09	1.09

* The signs are for $\bar{\alpha}'_{\text{Q}_i}$ in the order $i = 1, 2, 3, 4$.

^b $\Delta = |\bar{\alpha}'_{\text{u}^6\text{Li}} - \bar{\alpha}'_{\text{u}^7\text{Li}}|$

^c $\Sigma(\Delta)$ is the sum of Δ 's for each set.

for eliminating all but one of the sets. These criteria are now considered in turn.

(1) The sign of $\bar{\alpha}'_{CC}$: Yoshino and Bernstein²⁷ have presented convincing arguments based on differences between atomic and molecular polarizabilities, for believing that the sign of $\bar{\alpha}'_{CC}$ is positive in ethane and neopentane. It is unreasonable to expect that the sign would change for *t*-butyllithium. Table VIII lists the eight sets of solutions which give positive values for $\bar{\alpha}'_{CC}$. (The remaining eight sets are obtained by changing all signs.)

(2) Isotope invariance: The values of $\bar{\alpha}'_u$ should be invariant to isotope substitution. Table VIII shows the comparison for (*t*-Bu⁶Li)₄ and (*t*-Bu⁷Li)₄. The agreement is distinctly better for sets 5–8, in which the signs for $\bar{\alpha}'_{Q_2}$ and $\bar{\alpha}'_{Q_3}$ are the same, than for sets 1–4, in which these signs differ.

A further test is provided by the isotopic ratios $\bar{\alpha}'_{Q_2}$ and $\bar{\alpha}'_{Q_3}$, these two modes being the only ones predicted from the eigenvectors (Table VII) and found experimentally to show significant intensity changes between (*t*-Bu⁶Li)₄ and (*t*-Bu⁷Li)₄. The experimental ⁶Li/⁷Li ratios are 0.97 for $\bar{\alpha}'_{Q_2}$ and 1.09 for $\bar{\alpha}'_{Q_3}$. The ratios predicted from eq. (1) are shown in Table VIII for the different sets of $\bar{\alpha}'_u$'s. Again the clear superiority of sets 5–8 is evident, and sets 1–4 may be rejected.

(3) The magnitude of $\bar{\alpha}'_{CCC}$: Sets 1, 2, 5 and 6, which have the same sign for $\bar{\alpha}'_{Q_3}$ and $\bar{\alpha}'_{Q_4}$ may be rejected with confidence because they give $\bar{\alpha}'_{CCC}$ values much higher than the usual range for angle bending polarizability derivatives. The remaining four sets (opposite signs for $\bar{\alpha}'_{Q_3}$ and $\bar{\alpha}'_{Q_4}$) give $\bar{\alpha}'_{CCC}$ in the normal range. Comparable values have been obtained, for example, for (CH₃)₆M₂ (M = Si, Ge, Sn)²⁸ with $\bar{\alpha}'_{CMC} = -0.05$ to -0.21 \AA^2 .

(4) The magnitude of $\bar{\alpha}'_{CC}$: We expect $\bar{\alpha}'_{CC}$ to have a value characteristic of ordinary carbon-carbon single bonds. For neopentane $\bar{\alpha}'_{CC} = 1.17 \text{ \AA}^2$ while for ethane two estimates have been given, 1.37 or 0.93 \AA^2 depending on a choice of force fields. Sets 2, 4, 6 and 8 in Table VIII (same sign for $\bar{\alpha}'_{Q_1}$ and $\bar{\alpha}'_{Q_3}$) have $\bar{\alpha}'_{CC}$ comparable to these values, while sets 1, 3, 5 and 7 (opposite signs for $\bar{\alpha}'_{Q_1}$ and $\bar{\alpha}'_{Q_3}$) give values twice as high. If anything $\bar{\alpha}'_{CC}$ is underestimated in the present calculation. The neglect of the methyl rocking mode in the normal coordinate analysis is likely to produce an overestimate not only in the CC stretching force constant (see previous section) but also in the CC eigenvector element in Q₁. Since the methyl rocking coordinate is expected to have a very low associated polarizability derivative, it

would not contribute significantly to $\bar{\alpha}'_{Q_1}$, and an overestimate of the CC eigenvector element would produce an underestimate of $\bar{\alpha}'_{CC}$. Consequently sets 1, 3, 5 and 7 may be rejected.

A point of some interest is that solutions which give acceptable magnitudes for $\bar{\alpha}'_{CCC}$ and $\bar{\alpha}'_{CC}$ (sets 4 and 8) require that $\bar{\alpha}'_{LiC}$ be negative. As mentioned above a positive sign can be attached to $\bar{\alpha}'_{CC}$ with some confidence. Physical reasoning suggests that bond polarizability derivatives should ordinarily be positive—the molecule's electron cloud should become more deformable as a bond is stretched—and a positive sign has usually been assumed. However in a study of the thiocyanate ion Taylor, Long and Plane²⁹ found that a reasonable value for $\bar{\alpha}'_{CN}$ required a negative sign for $\bar{\alpha}'_{CS}$. The situation here is similar: reasonable values for $\bar{\alpha}'_{CC}$ and $\bar{\alpha}'_{CCC}$ require a negative sign for $\bar{\alpha}'_{LiC}$.

The only solution which is acceptable on all four criteria is set 8.

CONCLUSIONS

By the preceding process of elimination we arrive at a solution to the intensity equations which provides reasonable polarizability derivatives for CC stretching and for CCC bending, and which demonstrates the expected invariance of bond polarizability derivatives to isotope substitution. This solution gives a value for $\bar{\alpha}'_{LiLi}$ which is only one-sixth that of $\bar{\alpha}'_{LiC}$ although the ratio of LiLi contacts to LiC contacts is one-half. The difference is accentuated by the expected proportionality to cube of the internuclear distance, predicted by the delta function potential equation of Long and Plane³⁰

$$\bar{\alpha}'_u = \frac{3}{2} \frac{g\sigma}{za_0} \left(\frac{n}{2}\right) r^3 \quad (2)$$

where r is the internuclear distance, $n/2$ is the number of electron pairs in the bond (bond order), a_0 is the Bohr radius, g is the delta function strength (estimated as $X^{1/2}$, where X is the Pauling³¹ electronegativity), σ is the Pauling covalent character $\exp(-\frac{1}{4}(X_A - X_B)^2)$ and z is the effective nuclear charge (taken as the atomic number minus the number of inner shell electrons). For heteronuclear bonds the geometric mean of g/z is taken.

Bond orders calculated with Equation (2) are 0.47 for C–C, 0.16 for Li–C and 0.008 for Li–Li. As has been emphasized elsewhere²⁸ Long and Plane bond orders cannot actually be taken to

count electron pairs, but they do provide a consistent basis for comparing related molecules. The carbon-carbon single bonds have associated values of 0.50 to 0.75 in ethane and neopentane. The usual range for metal-metal single bonds²⁸ is 0.3 to 0.4. It must be remembered, however, that there are only four bonding electron pairs in the entire Li_4C_4 cage of $(t\text{-BuLi})_4$, whereas there are six LiLi contacts. To get a rough idea of the number of electron pairs to be allocated to the Li_4 tetrahedron we might multiply $n/2_{\text{LiLi}}$ by six and divide by 0.35, an average value of $n/2$ for a single metal-metal bond. The result is $1/6$ electron pair for the Li_4 tetrahedron, leaving $3\frac{5}{8}$ electron pairs for the LiC bonds. The allocation of nearly all the bonding electrons to the LiC bonds is also consistent with the value of $n/2_{\text{LiC}}$, which is one-third of $n/2_{\text{CC}}$. A bond order of $1/3$ is expected for localized four-centered Li_3C bonds.

The Raman intensity measurements therefore strongly suggest that Li-Li bonding is not of great importance in $(t\text{-BuLi})_4$. Our best estimate is that something less than 5% of the bonding electron density in the Li_4C_4 cage is concentrated in the Li_4 tetrahedrons. This conclusion is consistent with an undetectably low ^6Li - ^7Li spin-spin coupling.¹³

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- There are actually five skeletal internal coordinates, with one redundancy in the A_1 block. The number of unknowns was reduced to four by setting $\bar{\alpha}'_{\text{LiCC}} = 0$. In the original bond polarizability theory of Wolkenstein²⁵ the reorientation of bonds was assumed to make no contribution to α'_Q . While this assumption was later shown to be needlessly restrictive,²⁶ experimental values for polarizability derivatives associated with angle bending coordinates have proved to be close to zero for a variety of molecules.^{23, 28}
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