moved in the unfolded form of the protein. In this form, at least for *Chromatium* HP_{red}, features inherent to clusters of the essential $[Fe_4S_4(S-Cys)_4]$ type exemplified by 2–5 begin to emerge. Spectral and redox properties of denatured Fd_{ox} proteins have not yet been reported. Future experiments will attempt to determine the effect of protein structure on active site properties. These are planned to include voltammetric and spectral studies of synthetic analogs derived from other cysteinyl peptides and of proteins under normal aqueous and denaturing conditions.
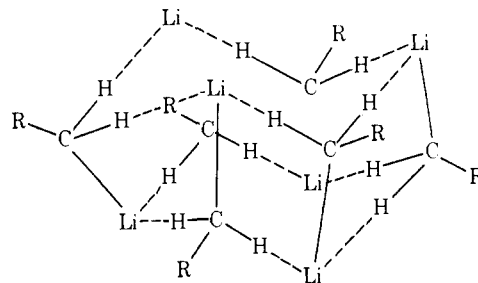
Stereochemistry of Polynuclear Compounds of the Main Group Elements. The Bonding and the Effect of Metal-Hydrogen-Carbon Interactions in the Molecular Structure of Cyclohexyllithium, a Hexameric Organolithium Compound[1]

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Abstract: A cyclohexyllithium benzene adduct, $[C_6H_{11}Li]_6(C_6H_6)_2$, has been isolated and characterized by infrared and single-crystal X-ray studies. As in other alkyllithium compounds, the C–H stretching frequency associated with the α-carbon atom is shifted to a lower frequency (2800 *vs.* 2900 cm^{-1} for cyclohexane). $[C_6H_{11}Li]_6(C_6H_6)_2$ crystals possess monoclinic symmetry, space group $P2_1/n$ with $a = 10.450$ (3) Å, $b = 10.443$ (4) Å, $c = 20.587$ (6) Å and $\beta = 92.40$ (1)°. The calculated density for 12 monomeric cyclohexyllithium groups and four benzene molecules per unit cell is 1.031 g/cm^3. A total of 2271 unique reflections were utilized to refine atomic parameters, including hydrogen atoms, to $R_F = 0.064$ and $R_{wF} = 0.048$. Cyclohexyllithium is hexameric with a crystallographic center of inversion. The molecular symmetry closely approximates S_6. The geometry of the lithium atoms is very similar to that observed for the copper atoms in $H_6Cu_6(PPh_3)_6$ and for the ruthenium atoms in $H_2Ru_6(CO)_{18}$, with the metal atoms in a near octahedral configuration. There are six triangular lithium atom faces which have two short (2.397 (6) Å) and one long (2.968 (9) Å) distance. The former lithium–lithium atom distances are the shortest known lithium–lithium atom contact. The α-carbon atom of each cyclohexyl group is most closely associated (2.184 (3) Å) with the two lithium atoms which possess the longest lithium–lithium atom distance. A vector from the α-carbon atom to the plane of the isosceles triangle intersects the plane at the midpoint of this shortest lithium–lithium atom bond. The orientation of the cyclohexyl group is apparently determined by the interaction of α and β protons with the lithium atoms. The lithium–carbon atom distances are 2.184 (3) and 2.300 (4) Å. The lithium–hydrogen atom distances are 2.00 (5), 2.09 (5), and 2.33 (5) Å. The two benzene molecules are situated above the two equilateral triangle lithium atom faces which are transoidal. The Li–Li atom distance in these faces is 2.968 (9) Å. The bonding of organolithium hexamers is discussed in terms of a localized four-centered bond which involves a triangle of lithium atoms and the bridging carbon atoms of an alkyl ligand.

I n all alkyllithium compounds which have been studied to date, the α-carbon C–H stretching modes have been shifted to a lower frequency relative to that of the parent hydrocarbon.[2] One possible explanation for this effect is the formation of three-center bonds of the form C$\cdots$H$\cdots$Li. The same model has been used as an explanation for the absence of ^{13}C–^{7}Li scalar coupling in hexameric *n*-butyllithium by Craubner,[3] as shown in the figure below. The results of neutron and X-ray diffraction studies of LiB(CH$_3$)$_4$[4] also suggest that lithium–hydrogen interactions may be important in the chemistry and stabilization of organolithium compounds. Li$\cdots$H$\cdots$C bonding may also be important in the structure of tetralithium octamethyl-

dichromium(II) tetrahydrofuranate.[5] In contrast, the published structural data for organoaluminum and organolithium compounds[6,7] and the fact that a dimin-

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ished C–H stretching frequency is observed for what is apparently monomeric CH_3Li isolated in a matrix[8] argue against $C\cdots H\cdots M$ interactions having any stereochemical importance in representative element organometallic compounds.

Probably the best organic group to use in order to investigate the structural aspects of the above effect is a secondary hydrocarbon. Unlike methyl-[9] and ethyllithium[10] in which extended three-dimensional interactions in the solid state make it impossible to study the bonding features of the isolated oligomeric units which are present in solution, secondary and tertiary organolithium compounds are relatively volatile and soluble in inert solvents such as benzene which suggests significantly decreased intermolecular interactions in the solid state. An added advantage is that the configuration about the α-carbon atom can be more precisely determined by X-ray analysis for a secondary hydrocarbon than for a primary hydrocarbon.

In this paper, the synthesis and infrared and structural characterization of cyclohexyllithium are described. A bonding scheme for hexameric polynuclear organolithium compounds is proposed, and the possible effects of C–H–Li bonding on the structural properties of cyclohexyllithium are discussed.

Experimental Section

A. **Synthesis and Isolation.** A three-neck round-bottom flask fitted with a reflux condenser, source of dry nitrogen, and a dropping funnel was flushed with dry nitrogen gas. After charging the flask with 500 ml of dry hexane and 6.94 g (1 mol) of lithium sand, 59.31 g (0.5 mol) of cyclohexyl chloride was added slowly. About 5 ml had been added before the reaction was initiated by heating slightly. Once the reaction had begun, the reaction pot was placed in an ice bath and the remainder of the cyclohexyl chloride was added at a rate to keep the reaction temperature about 20–30°. After the addition was complete, the reaction mixture contained a purple precipitate. Similar precipitates have been observed in other reactions in which alkali metals have been used.

The reaction mixture was then transferred to an argon-filled drybox and filtered yielding a clear colorless solution. The solid residue was extracted with hot benzene and a white crystalline solid was obtained upon evaporation of the solvent. The hexane solution yielded 8 g of cyclohexyllithium after cooling to 0°. The total yield was 10 g. Recrystallization from dry benzene gave crystals suitable for X-ray analysis. The crystals grew as colorless needles or bipyramids from benzene depending on the concentration.

B. **X-Ray Analysis. 1. Data Collection and Reduction.** Crystals of $C_6H_{11}Li\cdot(C_6H_6)$ suitable for X-ray analysis were sealed in thin-walled glass capillaries in an argon atmosphere because of their sensitivity to oxygen and water. Precession photographs showed that the needle-shaped crystals were monoclinic with absences for $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$, space group $P2_1/n$. Reflections with $l = 0$ and $h = 2n + 1$ were weak indicating a pseudo-a glide. Precession photographs revealed that the bipyramid-shaped crystals had fourfold symmetry; however, these samples were not studied further.

The lattice parameters ($T = 23°$, λ 0.71069 Å) were determined from a least-squares refinement of 12 carefully centered peaks on a Picker four-cycle diffractometer. The cell constants obtained were $a = 10.450$ (3) Å, $b = 10.443$ (4) Å, $c = 20.587$ (6) Å, and $\beta = 92.40$ (1)°. The calculated density for 12 monomeric cyclohexyllithium units and four benzene molecules per unit cell is 1.031 g/cm^3. An accurate measurement of the density could not be obtained due to the reactivity of this compound.

Intensity data were measured using Mo Kα radiation on a fully automated Picker four-circle diffractometer equipped with a highly oriented graphite single-crystal monochromator. A triangular-

shaped crystal 0.5 mm on a side and 0.3 mm thick and mounted with the a^* axis coincident with the axis of rotation was used for data collection. Data were collected using the θ–2θ scan technique with a scan rate of 1.0°/min and with a scan width of 1.8° being sufficient to collect all of the peak intensity. Stationary crystal–stationary counter background counts of 10 sec were taken at the beginning and at the end of each scan. A takeoff angle of 1.55° was used which provided approximately 80% of the intensity of a typically large peak. Pulse height analyzer settings of 3.0 and 8.0 for the lower and upper level discriminators, respectively, were used. Several ω scans showed the typical full peak width at half height to be approximately 0.15° indicating the mosaicity was acceptably low for data collection. Copper foil attenuators whose attenuation factors were known were automatically inserted in front of the counter aperture whenever the counting rate exceeded 10,000 counts per second in order to eliminate saturation of the counter circuit. Three standard peaks were monitored every 60 reflections to ensure crystal and counter stability.

A full form of data ($\bar{h}kl$ and hkl) was measured twice, and the two sets of data averaged to give a total of 3511 unique reflections ($2\theta_{max} = 48°$). The intensities were corrected for background and Lorentz-polarization, and structure factor amplitudes were calculated using the local program GORDO. The linear absorption coefficient was $\mu = 0.593$ cm^{-1} and the neglect of an absorption correction was estimated to give an error no greater than 1% in the corrected intensities. Of the unique data, 1149 reflections were considered observed (intensity three times the background) using the criteria $I_{obsd} \geq 3\sigma_c(I)$ where

$$\sigma_c(I) = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$$

as described previously.[11] All data, with values of $2\theta \leq 40°$, in addition to all observed reflections with $40° \leq 2\theta \leq 48°$ were used in the structure refinement (2271 reflections). Unobserved reflections in the region $40° \leq 2\theta \leq 48°$ were omitted in order to save computing time.

2. **Solution and Refinement of the Structure.** The solution of the structure was obtained by the symbolic addition method using the program package MULTAN.[12] After several cycles of refinement[13] on positional and isotropic temperature parameters, a value of R_2 (defined below) of 0.129 was obtained. A difference Fourier[14] calculation revealed the positions for all the hydrogen atoms. When the hydrogen atoms were included in the refinement, R_2 dropped to 0.088 at electron density levels of 0.7 ± 0.1 e/Å^3. No other extraneous peaks were observed with electron densities greater than 0.5 e/Å^3.

Unit weights were used in the refinement to this point. The final refinement was done using counting statistical weights

$$\sigma(|F|) = (|F|/2I)[T_c + 0.25(t_c/t_b)^2(B_1 + B_2) + (KI)^2]^{1/2}, \quad K = 0.03$$

In addition, all reflections having a negative F_{obsd} were set equal to zero and given an arbitrary σ of −20. After converting to anisotropic temperature factors for the non-hydrogen atoms and five cycles of full refinement of the non-hydrogen atoms and several cycles of isotropic refinement of the hydrogen atoms, the R factor converged[15] at

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.064$$
$$R_2 = (\Sigma w(F_o - F_c)^2/wF_o^2)^{1/2} = 0.048$$

The estimated standard deviation of an observation of unit weight was 1.62. A test of the counting statistics weighting scheme showed no systematic variation of $w(F_o - F_c)^2$ with the magnitude of the structure factors or with increasing sin θ/λ. A final difference Fourier map showed no peaks higher than 0.5 e/Å^3. The greatest residual electron density appeared in the regions slightly above the trigonal faces formed by the lithium atoms (see below).

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Table I. Positional Parameters for the Non-Hydrogen Atoms in $C_6H_{11}Li$

Atom	x	y	z
C(11)	−0.1822 (7)	0.0355 (4)	0.1584 (1)
C(12)	−0.0736 (7)	0.0778 (7)	0.1348 (2)
C(13)	−0.0212 (4)	0.1872 (8)	0.1581 (1)
C(14)	−0.0748 (8)	0.2477 (5)	0.2078 (3)
C(15)	−0.1821 (7)	0.2037 (7)	0.2306 (2)
C(16)	−0.2351 (4)	0.0964 (7)	0.2066 (3)
C(21)	−0.2459 (2)	0.0737 (2)	0.4716 (1)
C(22)	−0.2978 (3)	0.2051 (3)	0.4877 (1)
C(23)	−0.4354 (3)	0.2323 (3)	0.4694 (1)
C(24)	−0.4707 (3)	0.1981 (3)	0.4008 (2)
C(25)	−0.4310 (3)	0.0658 (3)	0.3838 (1)
C(26)	−0.2924 (2)	0.0401 (3)	0.4029 (1)
C(31)	0.0521 (2)	0.2481 (2)	0.4660 (1)
C(32)	0.1876 (3)	0.2886 (3)	0.4858 (1)
C(33)	0.2256 (2)	0.4255 (3)	0.4735 (2)
C(34)	0.1932 (3)	0.4659 (3)	0.4049 (2)
C(35)	0.0573 (3)	0.4384 (3)	0.3852 (1)
C(36)	0.0205 (2)	0.3013 (3)	0.3986 (1)
C(41)	−0.0665 (2)	0.0489 (2)	0.6249 (1)
C(42)	−0.1976 (3)	0.0164 (2)	0.6506 (1)
C(43)	−0.2204 (3)	0.0483 (3)	0.7201 (1)
C(44)	−0.1850 (3)	0.1848 (3)	0.7357 (1)
C(45)	−0.0532 (3)	0.2177 (3)	0.7163 (1)
C(46)	−0.0322 (3)	0.1824 (3)	0.6466 (1)
Li(1)	−0.0749 (4)	0.1523 (4)	0.5326 (2)
Li(2)	−0.0658 (4)	0.0808 (4)	0.4221 (2)
Li(3)	0.1504 (4)	0.0650 (4)	0.4630 (2)

Table II. Anisotropic Thermal Parameters $\times 10^4$ for the Non-Hydrogen Atoms in $C_6H_{11}Li$

Atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(11)	222 (9)	222 (7)	73 (2)	−46 (6)	1 (3)	−22 (3)
C(12)	217 (8)	315 (10)	51 (2)	25 (7)	11 (3)	−29 (4)
C(13)	186 (6)	358 (11)	56 (2)	−75 (8)	9 (3)	10 (4)
C(14)	329 (12)	203 (7)	56 (2)	−87 (8)	−19 (4)	3 (3)
C(15)	284 (10)	242 (9)	52 (2)	40 (7)	17 (4)	−22 (4)
C(16)	201 (7)	271 (9)	66 (2)	−29 (7)	31 (3)	−2 (3)
C(21)	124 (4)	089 (4)	25 (3)	1 (3)	8 (1)	6 (1)
C(22)	098 (4)	128 (4)	33 (1)	20 (3)	−3 (1)	1 (2)
C(23)	128 (4)	139 (4)	42 (1)	41 (3)	10 (2)	6 (2)
C(24)	098 (4)	201 (5)	44 (1)	19 (4)	−6 (2)	17 (2)
C(25)	124 (4)	188 (5)	35 (1)	0 (4)	−8 (2)	1 (2)
C(26)	101 (4)	149 (4)	37 (1)	4 (3)	−4 (2)	−11 (2)
C(31)	082 (3)	124 (4)	23 (1)	15 (3)	6 (1)	1 (1)
C(32)	154 (4)	098 (4)	31 (1)	5 (3)	2 (2)	1 (2)
C(33)	088 (3)	120 (4)	48 (1)	−16 (3)	5 (2)	−9 (2)
C(34)	165 (5)	096 (4)	49 (1)	−8 (4)	21 (2)	7 (2)
C(35)	166 (5)	134 (4)	34 (1)	5 (4)	5 (2)	8 (2)
C(36)	117 (4)	107 (4)	36 (1)	−3 (3)	4 (1)	3 (2)
C(41)	088 (3)	086 (3)	34 (1)	−1 (3)	4 (1)	−8 (2)
C(42)	132 (4)	100 (4)	32 (1)	4 (3)	7 (2)	1 (2)
C(43)	149 (4)	167 (5)	36 (1)	17 (4)	31 (2)	9 (2)
C(44)	201 (5)	168 (5)	26 (1)	−7 (4)	22 (2)	13 (2)
C(45)	192 (5)	140 (4)	34 (1)	23 (4)	15 (2)	20 (2)
C(46)	128 (4)	123 (4)	29 (1)	23 (3)	6 (1)	−1 (2)
Li(1)	126 (6)	112 (6)	31 (2)	4 (5)	9 (2)	−3 (2)
Li(2)	116 (6)	123 (6)	31 (2)	11 (5)	1 (2)	−0 (3)
Li(3)	95 (5)	121 (6)	33 (2)	−7 (5)	1 (2)	4 (3)

^{a} The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The scattering factors used in refinement for C^0 and Li^0 were taken from the compilation of Hanson, et al.,[16] and those for hydrogen are the best spherical form factors of Stewart, et al.[17] All refinement was carried out on an XDS Sigma 5 computer. Due to a rather small core storage, it was necessary to vary only half of the

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structure at one time. Two of the four rings and the lithium atoms were varied in each cycle.

The final positional and thermal parameters for the non-hydrogen atoms are contained in Tables I and II, respectively. Table III gives the hydrogen atom positions and thermal parameters.

Table III. Positional Parameters and Isotropic Thermal Parameters for the Hydrogen Atoms in $C_6H_{11}Li$

Atom	x	y	z	B^a
H(1)C(11)	−0.219 (2)	−0.042 (3)	0.147 (1)	9.2 (8)
H(1)C(12)	−0.042 (3)	0.046 (3)	0.104 (1)	9.8 (8)
H(1)C(13)	0.056 (3)	0.204 (3)	0.144 (1)	10.4 (9)
H(1)C(14)	−0.036 (3)	0.316 (3)	0.219 (1)	10.3 (8)
H(1)C(15)	−0.217 (3)	0.239 (3)	0.263 (1)	8.9 (8)
H(1)C(16)	−0.302 (2)	0.069 (3)	0.225 (1)	10.2 (8)
H(1)C(21)	−0.299 (2)	0.019 (2)	0.495 (1)	4.2 (5)
H(1)C(22)	−0.246 (2)	0.271 (2)	0.466 (1)	5.8 (6)
H(2)C(22)	−0.284 (2)	0.223 (2)	0.534 (1)	5.1 (6)
H(1)C(23)	−0.460 (2)	0.330 (2)	0.483 (1)	6.4 (6)
H(2)C(23)	−0.487 (2)	0.185 (2)	0.497 (1)	6.6 (6)
H(1)C(24)	−0.416 (2)	0.266 (2)	0.370 (1)	8.6 (7)
H(2)C(24)	−0.563 (2)	0.209 (2)	0.391 (1)	6.8 (6)
H(1)C(25)	−0.480 (2)	0.012 (3)	0.411 (1)	9.1 (7)
H(2)C(25)	−0.444 (2)	0.052 (2)	0.336 (1)	7.5 (7)
H(1)C(26)	−0.268 (2)	−0.048 (2)	0.389 (1)	6.4 (6)
H(2)C(26)	−0.243 (2)	0.093 (2)	0.370 (1)	7.8 (7)
H(1)C(31)	0.003 (2)	0.309 (2)	0.492 (1)	4.2 (5)
H(1)C(32)	0.245 (2)	0.240 (2)	0.461 (1)	5.3 (6)
H(2)C(32)	0.204 (2)	0.270 (2)	0.530 (1)	3.9 (5)
H(1)C(33)	0.316 (2)	0.443 (2)	0.483 (1)	6.1 (6)
H(2)C(33)	0.167 (2)	0.477 (2)	0.501 (1)	8.2 (7)
H(1)C(34)	0.250 (2)	0.418 (2)	0.377 (1)	7.3 (7)
H(2)C(34)	0.213 (2)	0.557 (2)	0.402 (1)	4.5 (5)
H(1)C(35)	0.037 (2)	0.458 (2)	0.341 (1)	6.9 (7)
H(2)C(35)	0.010 (2)	0.498 (2)	0.412 (1)	8.4 (7)
H(1)C(36)	0.071 (2)	0.258 (2)	0.368 (1)	4.7 (5)
H(2)C(36)	−0.072 (2)	0.293 (2)	0.385 (1)	6.0 (6)
H(1)C(41)	0.484 (2)	0.503 (2)	0.154 (1)	3.6 (5)
H(1)C(42)	0.241 (2)	0.435 (2)	0.124 (1)	4.9 (6)
H(2)C(42)	0.288 (2)	0.574 (2)	0.145 (1)	5.5 (6)
H(1)C(43)	0.190 (2)	0.469 (2)	0.232 (1)	6.7 (6)
H(2)C(43)	0.345 (2)	0.504 (2)	0.249 (1)	8.2 (7)
H(1)C(44)	0.311 (2)	0.301 (2)	0.283 (1)	7.4 (7)
H(2)C(44)	0.256 (2)	0.267 (3)	0.212 (1)	9.4 (8)
H(1)C(45)	0.510 (2)	0.343 (3)	0.243 (1)	8.9 (8)
H(2)C(45)	0.466 (2)	0.195 (2)	0.228 (1)	7.2 (6)
H(1)C(46)	0.412 (2)	0.251 (2)	0.122 (1)	4.8 (5)
H(2)C(46)	0.554 (2)	0.294 (2)	0.138 (1)	5.1 (6)

^{a} The form of the isotropic thermal parameter is $\exp[-B(\sin^2\theta/\lambda^2)]$.

Discussion

Molecular Structure. A considerable amount of information about the bonding and molecular properties of organolithium compounds has been obtained by methods other than X-ray analysis.[18] Although a detailed structure of an alkyllithium hexamer has not been reported, Brown and coworkers[19] have proposed a structure for the ethyllithium hexamer based on the results of the infrared and nuclear magnetic resonance (proton and lithium) spectra. From dielectric constant and molecular weight measurements of ethyllithium–triethylamine complexes in benzene solution, it has been demonstrated that tetramers and possibly hexamers are present in equilibrium in solution.[20,21]

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(20) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, 86, 2135 (1964).
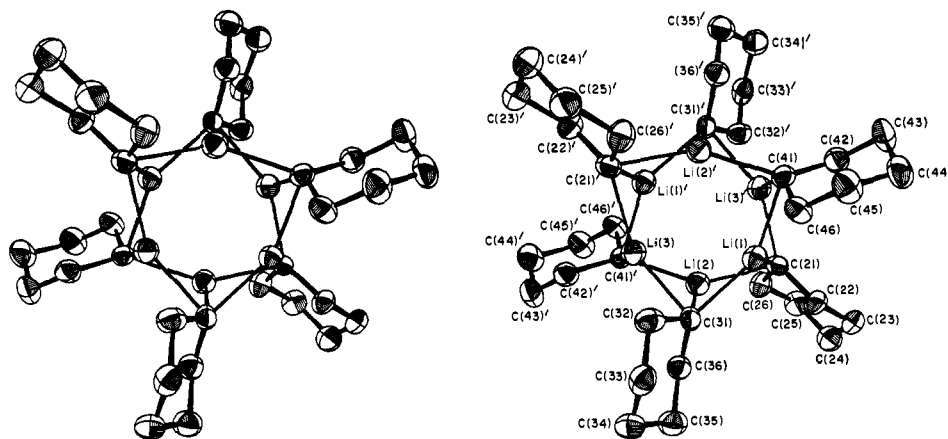(21) H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 92, 4664 (1970).

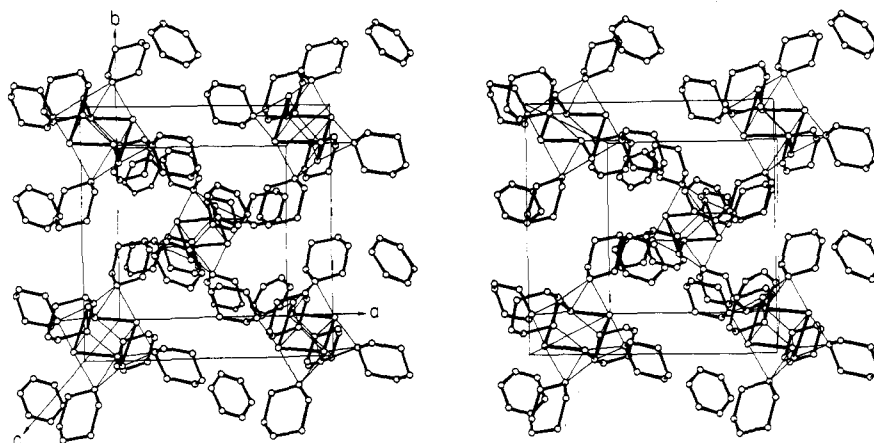**Figure 1.** Stereoscopic view of the molecular geometry of the $C_6H_{11}Li$ hexamer.

Figure 2. Stereoscopic view of the ab projection of the unit cell of $C_6H_{11}Li$.

The mass spectrum of ethyllithium vapor[22] reveals the presence of ions of the form $Li_nR_{n-1}^+$, $n = 1$–6. On the basis of appearance potentials, $Li_6R_5^+$ and $Li_4R_3^+$ are the only parent species in the vapor which would imply that in the vapor state Li_6R_6 and Li_4R_4 molecules are present in high concentrations.

The structure of cyclohexyllithium is essentially the same as the structure Brown[19] predicted for hexameric alkyllithium compounds and is shown in Figure 1. The projection of the unit cell is shown in Figure 2. The core of the molecule is a distorted octahedron of lithium atoms. The periphery of the molecule is made up of the cyclohexyl rings which bond into the six smaller of the eight triangular faces formed by the lithium core. The two benzene solvent molecules lie above and below the two larger transoid faces. The unit cell contains two symmetry related molecules which possess a center of symmetry (and approximate S_6 symmetry) and lie about the two inversion centers at $00^1/_2$ and $^1/_2{}^1/_20$ in the unit cell.

The interaction between the cyclohexyl rings and the lithium hexamer can best be explained by looking at the projection of the α and β carbons of the cyclohexyl rings on the lithium atom faces (Figures 3 and 4). The lithium atom face contains two short (av 2.397 (6) Å) lithium–lithium distances and one long (av 2.968 (9) Å) distance, where the values in parentheses are the stan-

(22) J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

dard deviation of the mean defined by $\sigma = [\Sigma^n(x_i - \bar{x})^2/(n-1)]^{1/2}$ or the average standard deviation given by $[\Sigma\sigma(x_i)/n]$, whichever is larger. The α-carbon atom is most closely associated (av 2.184 (3) Å) with the two lithium atoms which possess the longest lithium–lithium atom distance and is positioned almost above the midpoint of the line drawn between these two lithium atoms. The α-carbon atom is further from the third lithium atom in the face (av 2.300 (4) Å). The lithium–carbon–lithium atom angle which is formed by the two lithium atoms separated by a short lithium–lithium distance and the α-carbon is 64.6 (2)° (av). The lithium–carbon–lithium atom angle, which is formed by the two lithium atoms separated by a long lithium–lithium atom distance and the α-carbon atom, is 85.6 (3)° (av).

The cyclohexyl rings are in the chair form and are associated equatorially with the lithium atom faces. *The orientation of the cyclohexyl rings seems to be determined in part if not completely by the interaction of the α and β protons with the lithium atoms (Figure 5).* The complete coordination sphere around the lithium atom consists of three carbon and three hydrogen atoms. After correcting the hydrogen–carbon atom distances by setting them at 1.09 Å (C–H distance as determined by neutron diffraction studies of alkyl-containing compounds), the α-hydrogen–lithium atom distance is 2.003 Å (av) which is similar to the hydrogen–lithium atom distance of 2.043 (1) Å in lithium hydride in the
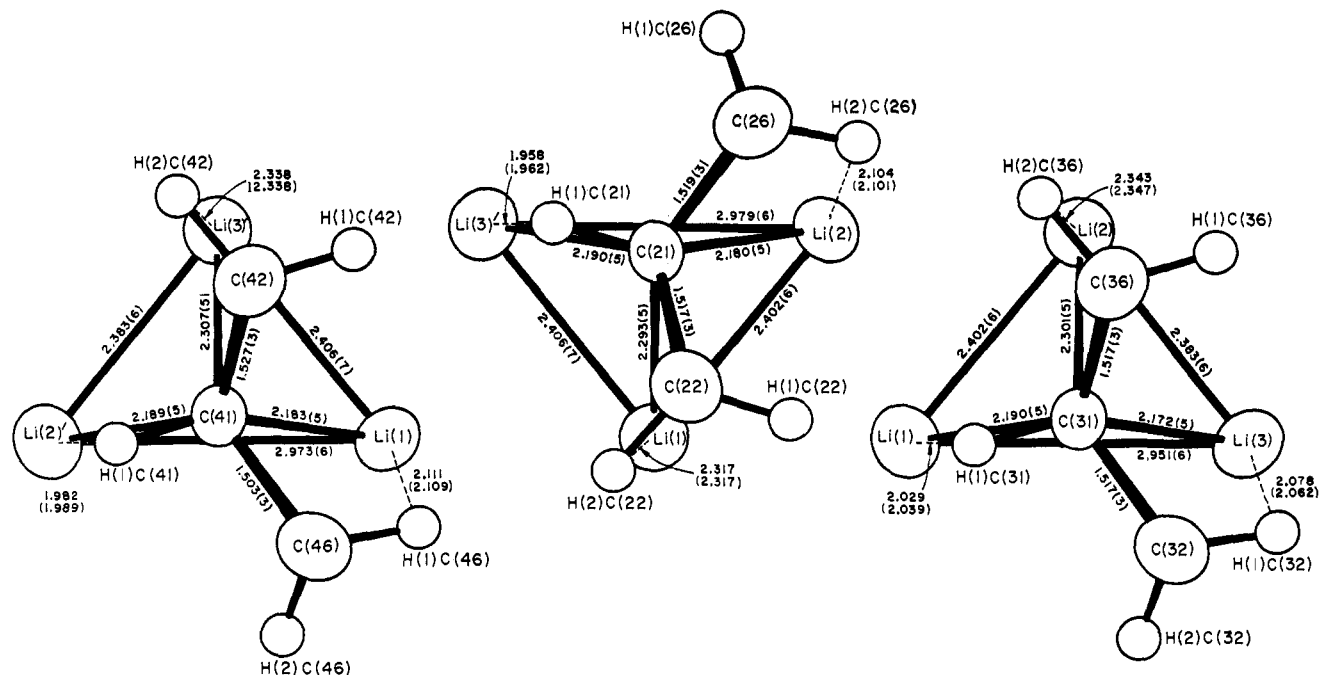
Figure 3. Projection of the α- and β-carbons on the lithium faces with distances.
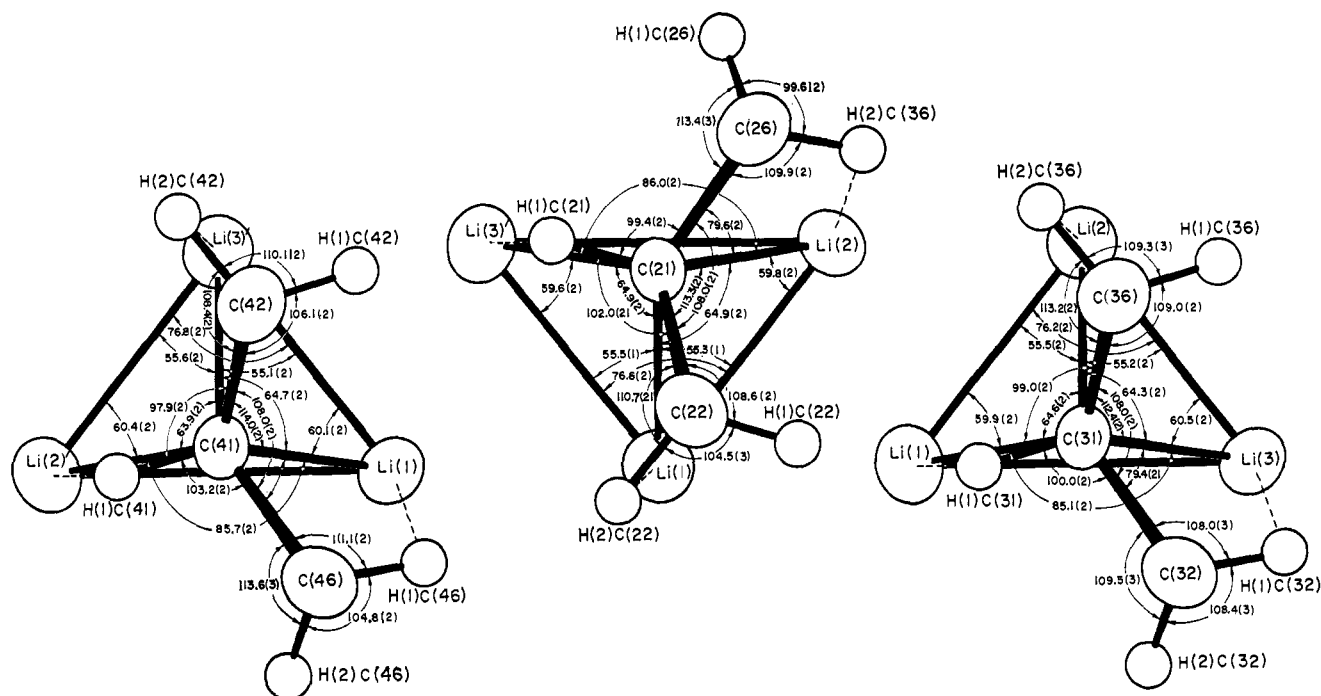

Figure 4. Projection of the α- and β-carbons on the lithium faces with angles.

solid state.[23] The β-hydrogen–lithium atom distances are 2.09 (1) (av) and 2.33 (1) Å (av). The fact that the α-hydrogen atom is always associated with one of the two lithium atoms which form the long edge in the lithium atom face means that the cyclohexyl rings are essentially perpendicular to the long lithium–lithium edge and that the R₂CH fragment is in a nearly *eclipsed* configuration with respect to the triangle of lithium atoms in the face to which the R₂CH group is coordinated.

The carbon–carbon atom bond distances and angles

(23) E. Zintl and A. Harder, *Z. Phys. Chem. Abt. B*, **28**, 478 (1935).

are given in Figure 6 for the three cyclohexyl rings. The ring carbon–carbon atoms distances range from 1.488 to 1.527 Å with an average of 1.505 (4) Å. The shorter than normal C–C bond lengths are attributed to ring thermal motions of the cyclohexane group. The angles in the rings range from 108.0 to 118.0°. The average value of the $C(\beta)$–$C(\alpha)$–$C(\beta)$ angles is 108.0 (2)°. The probability (χ^2 test) is less than 0.001 that this bond angle is physically identical with the other bond angles in the ring. The α-carbon atom should carry the most negative charge of any atoms in the cyclohexyl ring and the small $C(\beta)$–$C(\alpha)$–$C(\beta)$ angle
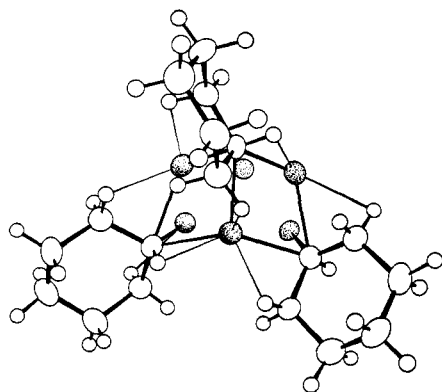
Figure 5. Coordination sphere of lithium atom.

does suggest enhanced p character in the orbitals used by the α-carbon atom to bond the β-carbon atoms. The torsional angles for the cyclohexyl rings are given in Table IV and average 48.8°.

Table IV. Torsional Angles (deg) for the Cyclohexyl Rings in $C_6H_{11}Li$

Atoms	Torsion angle
C(25)-C(26)-C(21)-C(22)	44.8
C(26)-C(21)-C(22)-C(23)	44.5
C(21)-C(22)-C(23)-C(24)	49.5
C(22)-C(23)-C(24)-C(25)	50.4
C(23)-C(24)-C(25)-C(26)	50.3
C(24)-C(25)-C(26)-C(21)	49.8
C(35)-C(36)-C(31)-C(32)	44.4
C(36)-C(31)-C(32)-C(33)	44.8
C(31)-C(32)-C(33)-C(34)	50.4
C(32)-C(33)-C(34)-C(35)	51.6
C(33)-C(34)-C(35)-C(36)	51.5
C(34)-C(35)-C(36)-C(31)	50.2
C(45)-C(46)-C(41)-C(42)	45.5
C(46)-C(41)-C(42)-C(43)	45.8
C(41)-C(42)-C(43)-C(44)	50.7
C(42)-C(43)-C(44)-C(45)	51.8
C(43)-C(44)-C(45)-C(46)	51.5
C(44)-C(45)-C(46)-C(41)	50.7

Figure 6. Interatomic distances (Å) and bond angles (deg) for the cyclohexyl rings in $C_6H_{11}Li$.

Brown[18,19,21] has suggested the possibility that the electron-deficient polymeric alkyllithium compounds might act as charge-transfer acceptors toward suitable bases of the π type. The benzene molecules do indeed occupy the open spaces above the large lithium faces in in the crystal lattice. The closest approach of the benzene molecule to the hexamer is 2.5 Å, the distance between H(1)–C(13) and H(2)–C(44). The average carbon–carbon bond length is 1.332 (6); however, the relatively high thermal motion of the ring probably resulted in artifically short carbon–carbon atom distances. The average deviation of the carbon atoms in the benzene ring from planarity is 0.011 Å. It should be possible for bases which are less bulky to associate even more strongly with the two "open" transoid lithium faces forming complexes of the general form (cyclohexyllithium)$_6$(base)$_2$. There is some evidence that such a complex is present in benzene solutions of ethyllithium and triethylamine at low amine–hexamer ratios. At higher amine–hexamer ratios, the hexameric units dissociate to solvated tetrameric units.[21]

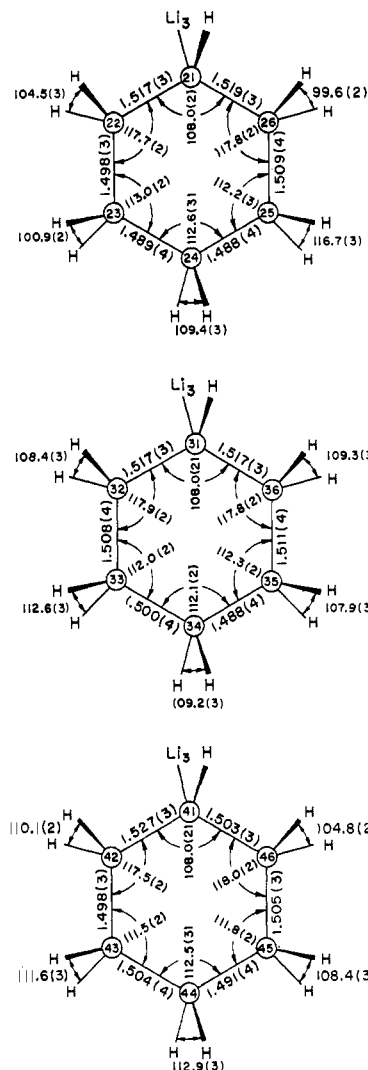To date, only three other detailed structural studies of alkyllithium compounds have been completed. The

structures of the unsolvated methyllithium[9] and ethyllithium[10] were completed early in the 1960's. More recently the structure of the solvated [1.1.0]bicyclobutyllithium has been reported.[7] Cyclohexyllithium is a hexamer whereas methyllithium[9] and ethyllithium[10] are both tetramers and bicyclobutyllithium·TMEDA[7] is a dimer. Because of the small steric requirements of the methyl group and the interaction of the lithium atoms with the methyl hydrogen atoms, there is a strong three-dimensional association among the tetrameric units in methyllithium. As in cyclohexyllithium, each lithium atom is surrounded by three carbon atoms and three hydrogen atoms. The increase in the steric requirements for an ethyl group results in an essentially linear association of tetrameric units in ethyllithium. In ethyllithium, there are two lithium–hydrogen atom distances of less than 2.09 Å. In cyclohexyllithium, the steric requirements permit the formation of hexameric units; however, the steric requirements and the hydrogen atom interactions satisfy the coordination sphere of the lithium atoms so that there is no association of the hexameric units. The lithium–lithium distances in cyclohexyllithium have average values of 2.397 (6) and 2.968 (9) Å compared to 2.424 (9), 2.603 (10), and 2.633 (8) Å for ethyllithium, 2.68 (5) Å for methyllithium, and
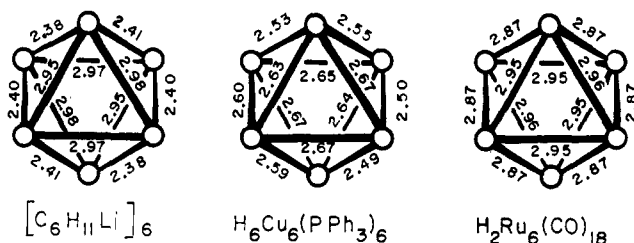
Figure 7. Metal–metal distances within the hexameric metal clusters $[C_6H_{11}Li]_6$, $H_6Cu_6(PPh_3)_6$, and $H_2Ru_6(CO)_{18}$.

2.74 (7) Å for bicyclobutyllithium. The lithium–lithium atom distance of 2.397 (6) Å in cyclohexyllithium is the shortest lithium–lithium distance known and considerably shorter than the observed value in the metal (3.04 Å). The lithium–carbon distances in cyclohexyllithium have average values of 2.184 (3) and 2.300 (4) Å compared to 2.188 (4) and 2.252 (6) Å for ethyllithium, 2.31 (5) and 2.36 (5) Å for methyllithium, and an average of 2.23 (5) Å for bicyclobutyllithium. The structures of two hexameric transition metal cluster compounds, which have been reported recently, show some similarities to the structure of cyclohexyllithium. The $H_2Ru_6(CO)_{18}$ cluster[24] (Figure 7) has C_1 symmetry (and approximate D_{3d} symmetry) with its six ruthenium atoms defining a distorted octahedron. Each ruthenium atom is associated with three terminal carbonyl ligands. The $H_6Cu_6(PPh_3)_6$ cluster[25] is distorted from regular O_h symmetry with each copper atom bonded to a triphenylphosphine ligand. The hydride ligands were not located but assumed to be bridging on the edge of the two large triangular faces. We propose that the hydride ligands in $H_6Cu_6(PPh_3)_6$ are located in positions similar to the positions of the α-carbons in cyclohexyllithium. In all three compounds the metal atom core is a distorted octahedron with the metal–metal bond lengths such that two transoid triangular faces are appreciably larger than the remaining six faces of the octahedron.

Spectroscopic Characterization. The infrared spectrum (Nujol mull, NaCl) of the cyclohexyllithium which was crystallized from the hexane solution gave the following frequency maxima: 2800, 2720, 1450, 1340, 1260, 1160, 1080, 1030, 1015, 980, 900, 850, 830, 790, 770, 675, 600, 570 cm^{-1}. This can be compared to the infrared spectrum of cyclohexane which gives the following frequency maxima: 2900, 2800, 2300, 1450, 1240, 1040, 1020, 900, 860, 792 cm^{-1}. In the spectrum of cyclohexyllithium the bands at 2800 and 2720 cm^{-1} can be assigned to the α-C–H stretching modes. As in all alkyllithium compounds studied thus far, the C–H stretching modes associated with the α position have been shifted to a lower frequency relative to that found in the parent hydrocarbons.[1] The bands corresponding to the remaining C–H stretching modes probably appear at 2900 and 2800 cm^{-1}. The band at 2900 cm^{-1} (asymmetric stretch) will be hidden under the large Nujol peak (cyclohexyllithium reacts with Fluorolube) in this region of the spectrum and the band at 2800 cm^{-1} (symmetric stretch) would overlap with the α-C–H band at 2800 cm^{-1} (asymmetric stretch). The bands between 1500 and 1000 cm^{-1} can be assigned to C–H deforma-

tions and the bands between 1000 and 650 cm^{-1} can be assigned to skeletal deformations. Compared to the parent hydrocarbon, the region between 1500 and 650 cm^{-1} in the spectrum of cyclohexyllithium is much more complex. This is probably due to the reduction in symmetry and the alteration of the cyclohexyl ring on bonding with the lithium atom.

The bands in the regions described above have been shown not to shift on isotropic substitution of the lithium[1] and therefore do not involve lithium vibrations. Bands which do involve the motion of lithium atoms have been found in the region 600–300 cm^{-1}, and it is on this basis that the bands found in cyclohexyllithium at 600 and 570 cm^{-1} may tentatively be assigned to C–Li absorptions.

Bonding. The bonding in alkyllithiums has been a subject of considerable interest since the discovery of their polymeric nature.[18] These oligomers are electron-deficient in the sense that there are more interatomic contacts than there are valence electron pairs available for bonding.[26] Localized four-centered bonds, involving a triangle of lithium atoms and the bridging carbon atom of an alkyl ligand, are consistent with the structures of methyllithium,[9] ethyllithium,[10] and cyclohexyllithium. Each four-centered bond would contain one electron pair, giving a lithium–carbon bond order of $^1/_3$. An alternate explanation is that there could be extensive electron delocalization in molecular orbitals extending over the entire alkyllithium cage[9] and therefore a relative large amount of lithium–lithium atom bonding.

Semiempirical molecular orbital calculations lend support to significant lithium–lithium bonding by giving lithium–lithium atom overlap populations comparable to those of the lithium–carbon bonds.[27,28] Also supporting a significant lithium–lithium bonding is the observation that the lithium atom clusters exhibit remarkable stability in mass spectral fragmentation patterns.[22,29]

Localized four-centered bonds with a small degree of lithium–lithium bonding are favored by the results of Brown, et al.[30] They were unable to detect any ^{6}Li–^{7}Li nuclear spin coupling in either methyl- or tert-butyllithium and estimated that the coupling constant was less than 3% of what might reasonably be expected for a full lithium–lithium bond. Consistent with these conclusions are the results from a normal coordinate analysis of the Raman intensities of $(t\text{-BuLi})_4$[31] which strongly suggest that lithium–lithium bonding is not of great importance in $(t\text{-BuLi})_4$. Scovell, et al.,[31] estimate that less than 5% of the bonding electron density, in the Li_4C_4 cage is concentrated in the Li_4 tetrahedrons. A recent ab initio calculation suggests a relatively small value for the lithium–lithium overlap populations in tetrameric $(LiCH_3)_4$[32] in contrast to a significant Li–Li overlap population for the hypothetical dimer (Li–

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$CH_3)_2$.[33] Unfortunately, no optimization of the molecular geometry of $(LiCH_3)_4$ was carried out and the long Li–Li distance of 2.68 Å which was used in the theoretical calculations may be largely the result of the intermolecular interactions for $(LiCH_3)_4$ in the solid state. Suggestive, but not conclusive, evidence for the localized four-centered bond theory is the fact that in the final difference Fourier of cyclohexyllithium the largest amounts of electron density were found above each of the six smaller triangular faces and about 0.77 Å below the α-carbons associated with the lithium atom faces. The residual electron density (0.50 ± 05 e/Å³) was located at the positions one would predict to be the centers of the four-centered bonds. The maximum electron density found elsewhere was 0.38 e/Å³.

Because of the substantial evidence supporting the four-centered bond theory, the bonding proposed for cyclohexyllithium is based on the four-centered bond theory and is pictorally displayed in Figure 8. The lithium atoms are proposed to be sp^2 hybridized. The sp^2 orbitals lie approximately in the plane of the large lithium atom faces. Two of the sp^2 orbitals are directed toward two bonding centers and the third orbital is not involved in bonding. The remaining p orbital is approximately perpendicular to the large lithium atom faces and has one of its lobes directed toward the third bonding center in which the lithium atom participates. The other lobe of the p orbital points upward from the large lithium atom face and is available to interact with bases which may associate with the "open" faces in organolithium hexamers. The vacant sp^2 and p

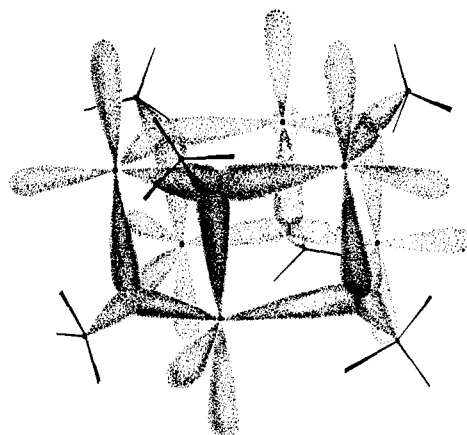(33) N. C. Baird, R. F. Barr, and R. K. Datta, *J. Organometal. Chem.*, **59**, 65 (1973).

Figure 8. Proposed bonding in the $C_6H_{11}Li$ hexamer.

orbitals may also interact with the α- and β-hydrogen atoms resulting in coordinatively saturated lithium atoms. Therefore, the four-centered bond results from the interaction of two sp^2 orbitals from two different lithium atoms, a p orbital from a third lithium atom, and an sp^3 orbital from an α-carbon atom.

A Correlation of Lithium-7 Chemical Shifts of Organolithium Derivatives with Structural Effects[1]

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received May 24, 1974

Abstract: The ⁷Li chemical shifts of a variety of organolithium derivatives have been determined using an internal proton lock as reference. Chemical shifts obtained in this manner are free of error due to magnetic susceptibility factors and provide the basis for a general standard of comparison by which all ⁷Li data may easily be correlated. Calculations were made in order to estimate the contributions of shielding terms that determine the ⁷Li chemical shifts. The results of these calculations show a reasonable correlation between the ⁷Li chemical shift and the substituent magnetic anisotropy term.

The nature of organolithium derivatives is reasonably well established and has been the subject of extensive reviews.[3–7] An increasingly important tool in

(1) This work was supported in part by the National Science Foundation Grants G. P. 8323 and G. P. 19299.
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these investigations has been the use of ⁷Li nuclear magnetic resonance.[4,5]

Brown, *et al.*,[8] were the first to use ⁷Li techniques in the study of organolithium derivatives. A surprisingly sharp resonance line for ethyllithium in benzene was observed at −1.00 ppm from a 70% solution of aqueous LiBr. West and Weiner[9] used ⁷Li nmr to establish the existence of one of the first mixed organolithium species

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