Journal of Organometallic Chemistry, 59 (1973) 65–81

THE BONDING, STRUCTURE AND ENERGETICS OF $LiCH_3$, $HBeCH_3$, $HBeNH_2$ AND THEIR DIMERS: *Ab initio* MOLECULAR ORBITAL CALCULATIONS*

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(Received January 18th, 1973)

SUMMARY

Single-determinant SCF–LCAO–MO calculations by the "*ab initio*" method are reported for $LiCH_3$, $HBeCH_3$, $HBeNH_2$ and their dimers (bridging between metal atoms by C, C, and N respectively). The structure for the $LiCH_3$ monomer agrees well with that anticipated by Andrews. Hyperconjugation to the metal atom is found to vary in the order $HBeNH_2 > HBeCH_3 > LiCH_3$. The optimum Li–C bond length in $(LiCH_3)_2$ of 2.31 Å agrees with that found from X-ray diffraction studies of $(LiCH_3)_4$, but the predicted Li–Li separation of 2.15 Å in the dimer is much less than found for the tetramer. The predicted dimerization energies (uncorrected for changes in electron correlation) for $LiCH_3$, $HBeCH_3$, and $HBeNH_2$ are 34.9, −3.8 and 60.6 kcal/mol of dimer respectively. An empirical theory of the bonding and energetics in alkyllithium aggregates is proposed; predictions using this simple model are in semiquantitative agreement with both the *ab initio* calculations and with the known properties of such compounds.

INTRODUCTION

The aim of this study is to explore, by *ab initio* molecular orbital calculations, the bonding, geometrical structures and energetics of some "covalent" compounds of lithium and beryllium. The tendency of such systems to form aggregates (or in solution, to coordinate with solvent molecules) has often made difficult the experimental determination of the structure and monomer–polymer energetics. Semi-empirical MO methods are particularly unsuited to the calculations of wavefunctions for the polar bonds such as are present in these molecules, and their use in this context has led to conflicting and often bizarre predictions. For example, semi-empirical MO theory estimates of the dimerization energy for $LiCH_3$ range from a stabilization of ≈400 kcal/mol (CNDO/2 calculations[2a]) to a destabilization of ≈12 kcal/mol

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* Publication No. 78 of the Photochemistry Unit. Research supported by the National Research Council of Canada.

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(Extended Hückel calculations[2b]), and predictions of the valence-shell electron density of lithium in the monomer range from 0.63 (CNDO/2[2a]) to −0.11 electrons (Extended Hückel[2b]).

In the present report, *ab initio* calculations are employed to deduce the nature of the bonding (*e.g.* ionic versus covalent character, degree of hyperconjugation operative, etc.), the nature of the monomer–monomer interactions, and the optimum geometries for $LiCH_3$, $HBeCH_3$, $HBeNH_2$ and their respective dimers. While this paper was being prepared for submission, Guest, Hillier, and Saunders (GHS) reported *ab initio* calculations for the $LiCH_3$ monomer and tetramer[3]; however, no optimization of molecular geometry for either system was attempted in their calculations.

METHOD OF CALCULATION

The wavefunctions and energies reported herein were determined by single-

TABLE 1

STO EXPONENTS

Molecule	*Atom*	*Orbital*	*Exponent*
$LiCH_3$[a]	Li	1*s*	2.6906
		2*s*, $2p_\sigma$, $2p_\pi$	0.76
	C	1*s*	5.6727
		2*s*, 2*p*	1.62
	H	1*s*	1.25
$HBeCH_3$[b]	Be	1*s*	3.6848
		2*s*, $2p_\sigma$	1.12
		$2p_\pi$	0.75
	C	1*s*	5.6727
		2*s*, 2*p*	1.68
	H[d]	1*s*	1.24
	H[e]	1*s*	1.12
$HBeNH_2$[c]	Be	1*s*	3.6848
		2*s*, $2p_\sigma$	1.12
		$2p_\pi$	0.82
	N	1*s*	6.6651
		2*s*, $2p_\sigma$, $2p_{\sigma'}$	1.92
		$2p_\pi$	1.79
	H[f]	1*s*	1.24
	H[e]	1*s*	1.12

[a] Valence-shell orbital exponents are the result of an optimization procedure using only a 1*s*, 2*s* basis set for Li. [b] Exponent for 1*s* orbital of the H atom bonded to Be is the value found to be optimum for BeH_2 (unpublished calculations), while for the orbitals of the methyl hydrogens the standard values suggested by Pople and co-workers[4] are employed. Valence-shell σ orbital exponents are those found to be optimum in a set of calculations on $HBeCH_3$ using a 1*s*, 2*s*, $2p_\sigma$ basis set for Be [R(Be–C) 1.70 Å]. Exponents for the $2p_\pi$ orbitals are those found to be optimum for $HBeCH_3$ using σ exponents discussed above. [c] Exponent for 1*s* orbital of the H atom bonded to Be is the BeH_2 optimum value, while for the orbitals of the amino hydrogens the standard values of Pople and coworkers[4] are employed. The Be and N exponents (except for the $2p_\pi$ orbitals) are optimum values from an optimization on $HBeNH_2$ ($2p_\pi$ orbitals included). Exponents for the $2p_\pi$ orbitals are those deduced from a partial optimization on $HBeNH_2$ using the σ exponents discussed above. [d] Bonded to C. [e] Bonded to Be. [f] Bonded to N.

determinant Hartree–Fock–Roothaan calculations in which all integrals required are evaluated explicitly (*ab initio* method). The minimal basis set consisted of 1*s*, 2*s*, $2p_x$, $2p_y$ and $2p_z$ functions centered at the carbon and nitrogen atoms, and a 1*s* function centered at each hydrogen; a variable number of orbitals centered at the metal atoms was employed (*vide infra*). All integrals over these atomic orbitals required for the SCF molecular orbital calculations were evaluated using the STO-NG expansions of Pople and co-workers[4]: STO-3G expansions were used in all monomer calculations and for the final wavefunction and energy determination for each dimer, whereas the more economical STO-2G expansions were used for dimer geometry optimizations*. The atomic orbital exponents employed are listed in Table 1; the exponents for the inner shells of Li, Be, C and N are those established to be optimum for the free atoms[5], whereas those for the valence-shell orbitals are the result of partial optimizations for the monomers (see footnotes *a*, *b*, *c* of Table 1 for details). In all calculations, C–H bond lengths of 1.094 Å and tetrahedral HCH angles were assumed**.

RESULTS AND DISCUSSION

The $LiCH_3$ monomer

Since the only experimental information available to date concerning the

TABLE 2

SCF WAVEFUNCTION FOR $LiCH_3$

AO		*MO*						
		$1a_1$	$2a_1$	$3a_1$	$1e$		$4a_1$	$5a_1$
Li	1*s*	0.0001	0.9922	−0.0288	0.0	0.0	−0.1603	−0.1881
	2*s*	−0.0043	0.0315	0.0165	0.0	0.0	0.4586	0.7934
	$2p_x$	0.0	0.0	0.0	−0.0002	0.0535	0.0	0.0
	$2p_y$	0.0	0.0	0.0	−0.0535	−0.0002	0.0	0.0
	$2p_z$	0.0053	0.0046	−0.0056	0.0	0.0	−0.2542	0.5948
C	1*s*	0.9931	−0.0013	−0.2064	0.0	0.0	−0.0354	0.0246
	2*s*	0.0364	0.0032	0.6636	0.0	0.0	0.1178	−0.0871
	$2p_x$	0.0	0.0	0.0	−0.0022	0.5638	0.0	0.0
	$2p_y$	0.0	0.0	0.0	−0.5638	−0.0022	0.0	0.0
	$2p_z$	−0.0017	0.0044	−0.0918	0.0	0.0	0.6892	−0.2032
H	1*s*	−0.0065	−0.0020	0.1979	0.0019	−0.4776	−0.1331	0.0295
H′	1*s*	−0.0065	−0.0020	0.1979	−0.4146	0.2372	−0.1331	0.0295
H″	1*s*	−0.0065	−0.0020	0.1979	0.4127	0.2404	−0.1331	0.0295
Energy (a.u.)		−10.9745	−2.3451	−0.7989	−0.4410		−0.2369	+0.0677
		Total energy −46.41778 a.u.						

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* Integrals over Gaussian orbitals were evaluated using the IBMOL program of E. Clementi and D. R. Davis, as modified by W. A. Sanders, Catholic University of America, Washington. Calculations were executed on the University of Western Ontario CDC6400 computer.

** A series of model calculations on $LiCH_3$ yielded an optimum HCH angle of 108°, *i.e.* within 2° of the tetrahedral value, in agreement with the infrared spectral study of the $LiCH_3$ monomer in an argon matrix[1].

structure of the $LiCH_3$ monomer consists of an infrared spectrum in a solid argon matrix[1], energy minimization calculations were undertaken to establish the Li–C bond distance. Using a full set of (three) $2p$ orbitals on lithium, the optimum bond distance in the monomer is predicted to be 2.05 Å; although this value is considerably shorter than that of 2.31 Å found experimentally for the tetramer, it agrees well with the estimate of ≈2.10 Å anticipated by Andrews from considerations of covalent radii, force constants, etc.

In order to determine the portion of the Li–C bond energy which is due to a hyperconjugative "back-release" of electron density from the methyl unit to the lithium p_π orbitals, the total energy and bond distance were recalculated with only a $1s$, $2s$, $2p_\sigma$ orbital set for Li. Although the energetic destabilization due to the loss of the quasi-π bond is small (2.8 kcal/mol), the calculated bond length increases from 2.05 Å to 2.09 Å.

The SCF wavefunction, overlap populations, and both orbital and atomic gross populations for the full basis set calculation (Li–C distance 2.05 Å) are given in Tables 2, 3 and 4 respectively. Note that the electron density of 0.05 e associated with the lithium p_π orbitals amounts to 7% of the total Li valence population of 0.74

TABLE 3

OVERLAP POPULATIONS (ATOM–ATOM) IN $LiCH_3$

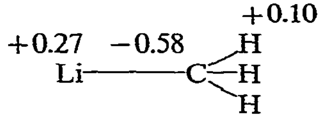
Atom pair	*Overlap population (in e)*
Li–C (σ)	+0.5119
Li–C (π)	+0.0444
Li–C (total)	+0.5563
Li–H (total)	−0.0644
C–H (avg.)	+0.7923
H–H'	−0.0374

TABLE 4

GROSS POPULATIONS FOR ORBITALS AND ATOMS IN $LiCH_3$

Atom	*Orbital(s)*	*Gross population (in e)*
Li	$1s$	1.9901
	$2s$	0.5030
	$2p_\sigma$	0.1858
	Total σ	2.6789
	$2p_x = 2p_y$	0.0252
	Total π	0.0504
	Total atomic	2.7293
C	$1s$	1.9935
	$2s$	1.2862
	$2p_\sigma$	1.2602
	$2p_x = 2p_y$	1.0204
	Total atomic	6.5807
H	$1s$	0.8967

electrons. The atomic net charges calculated by the two *ab initio* methods are in reasonable agreement with each other, and both are more in line with chemical intuition than are those predicted by the Extended Hückel Method:



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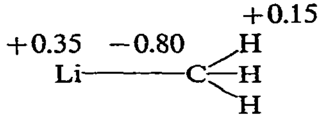

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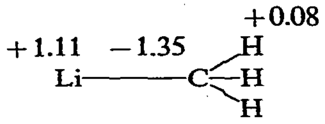
GHS[3]



Extended Hückel[2b]

Our *ab initio* charge distribution can be interpreted in terms of two-center, two-electron bonds if an ionic character of 27% is assigned to the lithium–carbon bond (as $Li^{\delta+}C^{\delta-}$) and an ionic character of 10% is assigned to each carbon–hydrogen linkage (as $C^{\delta+}H^{\delta-}$). This estimate is somewhat less than the 43% and 32% values which are based on Pauling electronegativities together with the ionicity equations of Pauling[6a] and of Hannay and Smyth[6b] respectively; the Mulliken *ab initio* value is however identical with that predicted by an electronegativity equalization method[7]. The dipole moment of 4.50 D calculated from the *ab initio* wavefunction is in good agreement with that of ≈6 D predicted by Andrews[1] from electronegativity and infrared spectrum arguments. All the estimates of Li–C bond ionicity from the *ab initio* calculations and electronegativity considerations are significantly larger than the charge separation of ≈0.1 e deduced from the ^{13}C NMR chemical shift for the methyllithium tetramer[8].

Inspection of the wavefunctions in Table 1 leads to the conclusion that the highest-occupied MO of the $LiCH_3$ monomer is essentially a σ(Li–C) bonding orbital. Vertical ionization from this orbital is predicted* to require some 6.4 eV, which is close to the experimental value for a lithium atom of 5.4 eV. Since the lowest-unoccupied orbital is predicted to be σ^*(C–Li) antibonding in character, the lowest excited singlet and triplet states (calculated transition energies of 82.0 and 54.6 kcal/mol respectively) both have $\sigma\sigma^*$ character.

The $HBeCH_3$ monomer

There has been some speculation as to the degree of hyperconjugation or "back-release" of electrons from carbon to beryllium in dimethylberyllium**. The uncommonly high value of the C–Be–C asymmetric stretching frequency[10] and the predominance of monomers in the gas phase both suggest that hyperconjugative stabilization may compete successfully with polymerization and may amount to much as 10 kcal/mol. However, Almenningen *et al.*[11a] argue that since the C–Be bond length in dimethylberyllium is nearly the same as that in di-tert-butylberyllium (in which, on the basis of vibrational frequencies[10], no hyperconjugation is expected) π-bonding is unimportant. Extended Hückel calculations[12] support this latter conclusion yielding π-bond overlap populations which are less than 10% of the σ-bond overlap populations.

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* Comparison of the calculated to observed ionization and electronic excitation energy is deferred to the last section.

** For a review of organoberyllium chemistry see ref. 9.

To deduce the strength of this quasi π bond, calculations for $HBeCH_3$ have been carried out both with and without $2p_\pi$ orbitals in the basis set for beryllium. First, with the full $2p$ basis set on beryllium, two bond lengths, Be–C and H–Be were optimized by energy minimization and found to be 1.71 and 1.33 Å respectively. (The former value agrees well with electron diffraction values of 1.698 and 1.699 Å for dimethylberyllium[11a] and di-t-butylberyllium[11b] respectively.) Removal of both $2p_\pi$ orbitals from Be results in a destablization of 7.1 kcal/mol, and in a lengthening of the Be–C bond by 0.05 to 1.76 Å. The value of 7.1 kcal/mol determined here for the π-bond strength represents an upper limit for each of the corresponding bonds in dimethylberyllium since donation of electrons from two methyl groups should be less than additive.

The SCF wavefunction, overlap population and both orbital and gross populations for the monomer (using the full basis set) are given in Tables 5, 6 and 7 respectively. For comparison, the overlap, orbital and gross populations for the partial basis set (at the same Be–C bond length) are also included. The charge on the carbon atom is essentially constant in the two basis sets, while the decrease in electron density on Be without the p_π orbitals is reflected as an increase in electron density on the methyl hydrogens. The cyclic pattern of σ-withdrawal/π-donation is evident however, from the changes in carbon orbital populations on removal of the $2p_\pi$ orbitals of Be; *i.e.* an increase of electron density in the $2p_x$ and $2p_y$ orbitals with a concomitant decrease in the $2s$ and $2p_z$ orbitals.

Interpreting the charge distribution in $HBeCH_3$ in terms of two-centre, two-electron bonds results in an ionic character of 15% for the H–Be bond (as $H^{\delta-}Be^{\delta+}$) and 13% for the Be–C bond (as $Be^{\delta+}C^{\delta-}$). These estimates of bond ionicity indicate that the Be–C linkage has about one-half the ionic character of the Li–C

TABLE 5

SCF WAVEFUNCTION FOR $HBeCH_3$

AO		*MO*								
		$1a_1$	$2a_1$	$3a_1$	$1e$		$4a_1$	$5a_1$	$2e$	
Be	$1s$	0.0002	0.9920	−0.0477	0.0	0.0	−0.1929	0.0825	0.0	0.0
	$2s$	−0.0053	0.0322	0.0602	0.0	0.0	0.4598	−0.2274	0.0	0.0
	$2p_x$	0.0	0.0	0.0	0.0821	−0.0001	0.0	0.0	−0.0080	−1.0290
	$2p_y$	0.0	0.0	0.0	0.0001	0.0821	0.0	0.0	1.0290	−0.0080
	$2p_z$	0.0076	0.0004	−0.0580	0.0	0.0	0.1783	0.4251	0.0	0.0
H(Be)	$1s$	−0.0021	−0.0042	0.0107	0.0	0.0	0.5580	0.2472	0.0	0.0
C	$1s$	0.9922	−0.0006	−0.2163	0.0	0.0	−0.0019	0.0260	0.0	0.0
	$2s$	0.0394	−0.0017	0.6481	0.0	0.0	0.247	−0.0651	0.0	0.0
	$2p_x$	0.0	0.0	0.0	0.5594	−0.0008	0.0	0.0	−0.1500	0.0012
	$2p_y$	0.0	0.0	0.0	0.0008	0.5594	0.0	0.0	0.0012	0.1500
	$2p_z$	0.0003	0.0003	−0.0450	0.0	0.0	0.2278	−0.6008	0.0	0.0
H(C)	$1s$	−0.0066	−0.0018	0.1917	0.4750	−0.0007	−0.0567	0.1492	−0.2095	0.0016
H'(C)	$1s$	−0.0066	−0.0018	0.1917	−0.2369	0.4117	−0.0567	0.1492	0.1062	0.1806
H''(C)	$1s$	−0.0066	−0.0018	0.1917	−0.2381	−0.4110	−0.0567	0.1492	0.1033	−0.1822
Energy (a.u.)		−11.0247	−4.5414	−0.8851	−0.5163		−0.4503	−0.3949	+0.1214	
		Total energy −54.16140 a.u.								

TABLE 6

OVERLAP POPULATIONS (ATOM–ATOM) IN $HBeCH_3$

Atom pair	*Overlap population (in e)*	
	With p_π	*Without p_π*
Be–C (σ)	0.6912	0.6926
Be–C (π)	0.0902	
Be–C (total)	0.7814	0.6926
H^a–Be	0.8175	0.8174
Be–H^b (avg)	−0.0417	−0.0712
C–H^b (avg)	0.7601	0.7867
H^a–H^b	0.0002	0.0002
H^b–H^b	−0.0339	−0.0368

[a] Bonded to Be. [b] Bonded to C.

TABLE 7

GROSS POPULATIONS FOR ORBITALS AND ATOMS IN $HBeCH_3$

Atom	*Orbital(s)*	*Gross population (in e)*	
		With p_π	*Without p_π*
Be	1s	1.9933	1.9934
	2s	0.8336	0.8509
	$2p_\sigma$	0.7779	0.7917
	total σ	1.6115	1.6426
	$2p_x=2p_y$	0.0546	
	total π	0.1091	
	total atomic	3.7139	3.6360
C	1s	1.9933	1.9922
	2s	1.2402	1.2321
	$2p_\sigma$	1.1850	1.1510
	$2p_x=2p_y$	1.0059	1.0304
	total atomic	6.4303	6.4361
H^a	1s	1.1530	1.1528
H^b	1s	0.9012	0.9250

[a] Bonded to Be. [b] Bonded to C.

bond (27% by Mulliken populations). The overlap populations also reflect this trend of increasing covalent character, the increase being ≈0.2 e in going from Li–C to Be–C.

The $HBeNH_2$ monomer

In contrast to $LiCH_3$ and $HBeCH_3$, considerable π-bonding is expected in $HBeNH_2$ due to the delocalization of the (nitrogen) lone pair in the latter. In a derivative of this compound, the trimer of bis(dimethylamino)beryllium, an X-ray structure determination[13] indicates that the terminal Be is coplanar with the dimethylamine group, suggesting significant Be–N π bonding. Since model calculations for $HBeNH_2$ indicated that the molecule is planar and has an H–Be–N angle of 180°, the geometry search was conducted without further variation in these parameters. In addition, the H–N–H angle was assumed to be 112°. All bond lengths H–Be, Be–N and N–H were optimized; the values calculated are 1.33, 1.53 and 1.04 Å respectively.

Removal of the Be $2p_\pi$ orbital perpendicular to the molecular plane results in a loss in stability of 35.2 kcal/mol; the π bonding with the other Be $2p_\pi$ orbital is relatively unimportant, contributing only 2.5 kcal/mol to the total energy. The Mulliken population analyses given in Table 8 indicate that 0.32 electrons are transferred from nitrogen to beryllium in the formation of the π bond. The effect of σ withdrawal/π donation is more dramatic here than in $HBeCH_3$ partly because of the greater electronegativity of nitrogen and the correspondingly greater ionic character.

TABLE 8

GROSS POPULATIONS FOR ORBITALS AND ATOMS IN $HBeNH_2$

Atom	*Orbital(s)*	*Gross population (in e)*	
		With p_π	*Without p_π*
Be	1*s*	1.9930	1.9934
	2*s*	0.6828	0.7251
	$2p_\sigma$	0.6481	0.7007
	total σ	1.3309	1.4258
	$2p\pi_x$	0.3244	
	total atomic	3.6483	3.4192
N	1*s*	1.9954	1.9951
	2*s*	1.5670	1.5127
	$2p_\sigma$	1.2921	1.1994
	$2p\pi_x$	1.6756	2.0000
	$2p_y$	1.1279	1.0836
	total atomic	7.6580	7.7907
H^a	1*s*	1.1387	1.1418
H^b	1*s*	0.7775	0.8241

[a] Bonded to Be. [b] Bonded to N.

From the Mulliken population analysis, the ionicity of the Be–N bond is 21%, midway between the values for Be–C and Li–C bonds. As expected, the calculations predict that the nitrogen lone pair is not completely delocalized in $HBeNH_2$ and that the NH_2 group carries a substantial overall negative charge even when π bonding is operative.

The dimers

Although many alkyllithium and alkylberyllium compounds exist normally as aggregates or polymers, the amount of computer time required to execute *ab initio* calculations on systems such as $(LiCH_3)_4$ is very large. For this reason we have used the *dimer* as prototype for each type of polymeric system. The general structure assumed for the dimers is shown in Fig. 1; *i.e.* a ring with all non-hydrogen atoms coplanar,

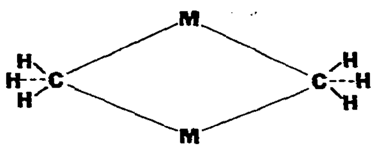

Fig. 1. General structure for dimers. Note that all M–C distances are assumed to be equal.

with all metal–carbon bond lengths equal and with all H–C–H bond angles and C–H bond lengths the same as those in the monomers. For reasons of economy, the metal 2*p* orbital (on Li or Be) which is perpendicular to the ring is *not* included in the basis set [in $(LiCH_3)_2$ and $(HBeCH_3)_2$ very little π bonding is expected].

Since no structural information exists for the $LiCH_3$ dimer, a limited search of the potential surface at the STO-2G level was undertaken to establish the optimum geometry. The geometric variables used in the search are the Li–C distance R_1 and the Li–Li distance R_2; for any set of values for R_1 and R_2, the carbon–carbon separation R_3 is uniquely determined ($R_3^2 = 4R_1^2 - R_2^2$). At all six points of the surface investigated (see Table 9), the dimer energy is found to be more negative (*i.e.* more stable) than that for two monomers calculated with the same basis set of orbitals (the monomer energy is -45.0353 a.u. under these conditions). In the first three calculations, the Li–Li distance is held constant at 2.56 Å, and the Li–C distance is varied. Using the optimum Li–C distance of 2.31 Å projected from these calculations, the Li–Li separation is varied. Although the optimum lithium–carbon separation of 2.31 Å deduced agrees exactly with the experimental value for the tetramer[14], the predicted lithium–lithium separation of 2.15 Å is much shorter than the 2.68 Å established for $(LiCH_3)_4$*. Rather short Li–Li distances have also been predicted for other dimeric lithium species, *e.g.* 2.36 Å in $(LiH)_2$ [15a] and 2.26 Å in $(LiF)_2$ [15b]. The Li–Li overlap population in the methyllithium dimer is more positive than that in the lithium hydride dimer[15a], in agreement with the predicted trend in Li–Li distances. As discussed later, significant Li–Li bonding and short Li–Li separations should *not* occur if the coordination number of lithium exceeds two. Thus it is not

TABLE 9

CALCULATED ENERGY FOR DIMER AT SEVERAL ASSUMED GEOMETRIES

R_1(Å)	R_2(Å)	R_3(Å)	*E* (a.u.)
2.09	2.56	3.30	−90.09884
2.20	2.56	3.58	−90.11791
2.28	2.56	3.77	−90.12399
2.31	2.46	3.91	−90.13030
2.31	2.36	3.97	−90.13407
2.31	2.21	4.06	−90.13669

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* In any complete geometry search, it would be necessary to redetermine R_1 using the new value of $R_2 = 2.15$ Å, followed by a redetermination of R_2 using the revised R_1, etc. Given the cost for each calculation, such a refinement of the structure is not justified at this time.

surprising that the Li–Li distances in alkyllithium tetramers and hexamers (Li coordination number >3) and in tetracoordinate systems such as bicyclo[1.1.0]but-1-yllithium tetramethylethylenediamine[16] (BLT) are found to be significantly longer than that predicted for $(LiCH_3)_2$.

Using the optimum STO-2G geometry ($R_1=2.31$ Å, $R_2=2.15$ Å, $R_3=4.09$ Å), the SCF wavefunction and energy for the dimer were calculated at the STO-3G level. The calculated energy of -92.88658 a.u. for $(LiCH_3)_2$ corresponds to a species which is 0.05557 a.u. (34.9 kcal/mol) more stable than two monomers (each calculated using the dimer basis set and the optimum monomer geometry for that basis set).

Since $(HBeCH_3)_2$ is used here as a prototype for polymeric dialkylberyllium systems, the methyl groups were assumed to bridge the Be atoms*. By analogy with the X-ray diffraction study of the $(CH_3)_2Be$ polymer[17], a Be–Be bond length of 2.09 Å and a Be–C bond length of 1.93 Å were assumed. The hydride hydrogens were assumed to be coplanar with the Be and C atoms of the ring, and to lie along the line defined by the Be–Be axis. Be–H distances of 1.33 Å were employed.

The calculated STO-3G energy differences between the dimer and two monomers (each calculated using a basis set which excludes one $2p_\pi$ orbital on Be) was found to be -3.8 kcal/mol; *i.e.* the dimer is predicted to be slightly *less* stable than are two isolated monomers. Although optimization of the dimer geometry would probably yield a small *positive* dimerization energy, such calculations were not executed since the overall magnitude of the dimerization energy will be dominated by the change in correlation energy**. All that one can say from the present calculations is that the dimerization energy of $HBeCH_3$ (for a methyl-bridged structure) is significantly less than for the $LiCH_3$ system.

The Mulliken atom–atom overlap populations and gross atomic populations for the dimers and for the corresponding monomers (in the same basis set and at the optimum metal–carbon bond lengths for that basis set) are compared in Tables 10–13.

The simplest explanation for the interactions between monomer units is electrostatic attraction between the partially-positive metal atom and the partially-

TABLE 10

ATOM–ATOM OVERLAP POPULATIONS IN $(LiCH_3)_2$ AND $LiCH_3$

Atom pair	*Total overlap population (in e)*		
	Monomer	*Dimer*	*Change*
Li–C (total)[a]	+0.5339	+0.5766	+0.0427
C–H (avg.)	+0.7983	+0.7837	−0.0146
Li–H (avg.)	−0.0708	−0.0280	+0.0428
Li–Li		+0.2778	+0.2778
C–C		−0.0016	−0.0016

[a] Li–C population is sum of Li_1–C_1 + Li_1–C_2 interactions

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* The ring with hydrogen atoms bridging the Be atoms should actually be more stable than the structure assumed.

** See also the changes in correlation energy upon polymerization of the BeH_2 systems as reported by Ahlrichs[18].

TABLE 11

GROSS ATOMIC POPULATIONS IN $(LiCH_3)_2$ AND $LiCH_3$

Atom	*Gross atomic population (in e)*		
	Monomer	*Dimer*	*Change*
Li	2.7184	2.6867	−0.0317
C	6.5793	6.6199	+0.0406
H (avg.)	0.9008	0.8978	−0.0030

TABLE 12

ATOM–ATOM OVERLAP POPULATIONS IN $(HBeCH_3)_2$ AND $HBeCH_3$

Atom pair	*Monomer*	*Dimer*	*Change*
Be–C (total)[a]	0.7237	0.7045	−0.0192
C–H (avg.)	0.7775	0.7629	−0.0146
H–Be	0.8169	0.8281	+0.0112
Be–Be		0.3222	+0.3222
C–C		−0.0222	−0.0222

[a] Be–C population is the sum of Be_1–C_1 and Be_1–C_2 interaction

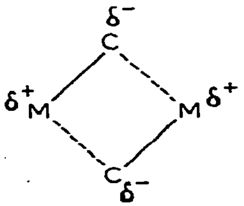
TABLE 13

GROSS ATOMIC POPULATIONS IN $(HBeCH_3)_2$ AND $HBeCH_3$

Atom	*Monomer*	*Dimer*	*Change*
Be	3.6641	3.6922	+0.0281
C	6.4288	6.4874	+0.0586
H[a]	1.1542	1.1668	+0.0126
H[b] (avg.)	0.9176	0.8846	−0.0330

[a] Bonded to Be. [b] Bonded to C.

negative methyl group:



Although it is impossible to "decompose" the total calculated energy to evaluate the magnitude of this effect, there are some indirect indications that "ionic" attraction does contribute significantly to the dimerization energy in $(LiCH_3)_2$ and to a lesser extent in $(HBeCH_3)_2$. First, the net charge on Li in the dimer is *more positive* than that in the monomer, while the net charge on the methyl group is *more negative* in the dimer than in the monomer*. This additional charge transfer of ≈0.03 electrons serves to increase the ionic stabilization, since the magnitude of the latter is roughly

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* Guest *et al.*[3] report a large increase in charge separation in going from the monomer to the tetramer.

proportional to the product of the excess charges on Li and C. For $(HBeCH_3)_2$ the increased charge transfer effect is not present. Second, an electrostatic calculation using point charges predicted by the Mulliken population analysis for the $LiCH_3$ dimer leads to an attractive interaction of 8.0 kcal/mol of dimer. A similar calculation for $(HBeCH_3)_2$ yields a smaller attractive interaction (4.9 kcal/mol).

In addition to the smaller amount of ionic attraction predicted for the $HBeCH_3$ dimer compared to $LiCH_3$, the change in covalent bond strength is also less favourable for the former than for the latter. For $(LiCH_3)_2$, the total Li–C overlap population increases by +0.043 e per C atom compared to the monomer (with both molecules considered at the appropriate optimum Li–C distances and using the same basis set), although this increase is offset by a decrease of −0.044 e in the total C–H overlap population. In contrast, the Be–C overlap population (per carbon) in the $HBeCH_3$ dimer is 0.019 e *less* than in the monomer, and the total C–H and Be–H overlap population decreases by 0.033 e*.

Although the metal–metal bond orders in both $(LiCH_3)_2$ and in $(HBeCH_3)_2$ are significantly positive, there are indications that this result will *not* carry over to the larger aggregates (at least in lithium systems):

(*i*). The experimental Li–Li distance of 2.68 Å in the tetramer is much longer than that of 2.15 Å predicted for the dimer[15].

(*ii*). Both the vibrational spectrum of $(t\text{-}C_4H_9Li)_4$[19] and the ^6Li–^7Li NMR spin–spin coupling constant for $(LiCH_3)_4$[8] predict a metal–metal bond order of close to zero.

(*iii*). The *ab initio* overlap population for $(LiCH_3)_4$ calculated by Guest *et al.*[3] is small in comparison to our value for the dimer (+0.05 *vs.* +0.28 respectively).

For comparison purposes, an STO-3G calculation has been carried out on $(HBeNH_2)_2$ using a geometry with the nitrogen atoms bridging, a Be–Be separation of 2.09 Å, and a Be–N bond length of 1.65 Å**. This system is more ionic than the Be–C system, resulting in greater charge separation and a more dramatic charge transfer (0.024 e) upon dimerization. The calculated dimerization energy of 60.6 kcal/mol is due primarily to the delocalization of the nitrogen lone pair via σ-bonding, an effect absent in the other systems. Note that the Be–N π bond (strength 35 kcal/mol) is broken upon dimerization. A comparison of the gross atomic populations and overlap populations for $(HBeNH_2)_2$ and its monomer are given in Tables 14 and 15; note the large increase in Be–N overlap population upon dimer formation.

As in the monomer, the MO's identified as Li–C bonding and Li–C antibonding in $(LiCH_3)_2$ are, respectively, less stable than all other occupied orbitals and more stable than all other unoccupied orbitals. Ionization from the least stable of the two dimer Li–C bonding MO's (which are split by 1.2 eV) is predicted to require 6.6 eV, slightly more than for the monomer***. Given that the appearance potential for

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* The lack of increase in covalent bond strength upon $HBeCH_3$ dimerization is associated to some extent with the inherent stability of the monomer via hyperconjugation, etc. The energy required to distort a $HBeCH_3$ monomer to the dimer geometry is 36.5 kcal/mol, compared to 11.8 kcal/mol for $LiCH_3$.

** Derived from ref. 13.

*** The increase in ionization potential from monomer to dimer is not an artifact of using different basis sets for the two cases, since recalculation of the monomer ionization potential using two 2*p* orbitals on Li also yields a value of 6.4 eV. Guest *et al.*[3] report ionization potentials of 6.8 eV and 7.0 eV for the monomer and tetramer respectively, in agreement with the monomer–dimer trend.

TABLE 14

GROSS ATOMIC POPULATIONS IN $(HBeNH_2)_2$ AND $HBeNH_2$

Atom	*Monomer*	*Dimer*	*Change*
Be	3.6483	3.6260	−0.0223
N	7.6580	7.6001	−0.0579
H[a]	1.1387	1.2038	+0.0651
H[b]	0.7775	0.7851	+0.0076

[a]Bonded to Be. [b]Bonded to N.

TABLE 15

ATOM-ATOM OVERLAP POPULATIONS IN $(HBeNH_2)_2$ AND $HBeNH_2$

Atom pair	*Monomer*	*Dimer*	*Change*
Be–N[a] (total)	0.8615	0.9890	+0.1275
N–H	0.7014	0.6960	−0.0054
H–Be	0.8195	0.7805	−0.0039
Be–Be		−0.2665	−0.2665
N–N		−0.0485	−0.0485

[a]Be–N population is the sum of Be_1–N_1 and Be_1–N_2.

$Li_4Et_3^+$ from Li_4Et_4 (*i.e.* the energy to ionize Li_4Et_4 *and* to break the $Li_4Et_3^+$ –Et bond) is 8.0 ± 0.5 eV[20], these ionization potentials are reasonable.

The most stable antibonding MO for the dimer is much higher in energy than in the monomer and the two Li–C antibonding MO's are only of slightly different energy. Consequently, the S_1 and S_2 states in the dimer (corresponding to excitations from the highest-occupied MO to the lowest unoccupied and second lowest unoccupied MO's respectively) are almost degenerate, and the calculated vertical transition energies from S_0 of 109.6 and 111.4 kcal/mol are both much larger than that for the monomer. (The corresponding triplet states T_1 and T_2, predicted to lie 99.5 and 105.9 kcal/mol above S_0, are split by a larger amount, and also require a much larger excitation energy than for the monomer.) Assuming that the theory in the next section is correct, a further shift to shorter wavelength is expected for the tetramer and the hexamer; in particular, the excitation wavelength for the latter systems is extrapolated as ≈ 200 nm. In agreement, the λ_{max} for hexameric ethyllithium in isooctane occurs at ≈ 210 nm[21].

It is instructive to compare the experimental energetics and excitation energy for LiC_2H_5. Given the $\Delta H_f^0(g)$ values[22] for LiC_2H_5, Li·, and C_2H_5· of +13.9, 38.4, and 26.0 kcal/mol respectively, the ΔH^0 for

$$1/n\ (LiC_2H_5)_n(g) \rightarrow Li\cdot + C_2H_5\cdot$$

is +50.5 kcal/mol. Since the heat of sublimation of LiC_2H_5 is 27.9 kcal/mol, the ΔH^0 to form gaseous Li· and C_2H_5· from solid LiC_2H_5 is 78.4 kcal/mol; although the ΔH_f^0 for LiC_2H_5 in alkane solution is not known presumably the ΔH^0 falls within the limits for the gas and solid reactant values. Thus excitation at 210 nm (*i.e.* 136

kcal/mol) supplies the ethyllithium aggregate with sufficient energy to break a Li–C bond, and the reaction

$$\mathrm{LiC_2H_5} \xrightarrow[210\ \mathrm{nm}]{h\nu} \mathrm{Li^{\bullet} + C_2H_5^{\bullet}}$$

is feasible from the S_1 (and presumably also the T_1) state. The presence of ethane gas[21] as a product in the photolysis of ethyllithium suggests that such homolytic bond dissociation does occur.

Theory of bonding and energetics in alkyllithium aggregates

Analysis of both the above calculations and the available experimental data for alkyllithium systems leads us to propose a simple working model for the bonding, energetics and structure of alkyllithium aggregates. (The same or a similar model is not applicable to alkylberyllium compounds due to their greater degree of covalency.)

Postulate 1: The bonding between the lithium atoms and the alkyl radicals in all LiR aggregate systems is sufficiently ionic in character (in the sense $\mathrm{Li^+R^-}$) that the total bonding energy of the aggregate is equal to the total number of nearest-neighbour $\mathrm{Li^+}$–$\mathrm{R^-}$ interactions times a constant ε($\varepsilon \approx 17$ kcal/mol when R=Me, Et)*.

Postulate 2: Although Li–R bonding is predominantly ionic, sufficient covalent character is present such that the number of nearest-neighbours surrounding each Li does not exceed four (*i.e.* the number of valence orbitals for Li atom)**.

Postulate 3: Excitation or ionization of a valence electron in an alkyllithium aggregate is a localized event in that (*a*) ionization of an electron from the $\mathrm{R^-}$ unit

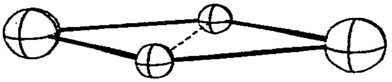

Fig. 2. Proposed structure for LiR dimers. The Li and R groups are represented by small and large balls respectively. Solid lines indicate nearest-neighbour (bonding) Li–R interactions; broken lines are used to join Li atoms.

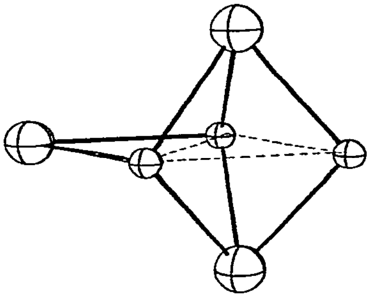

Fig. 3. Proposed structure for LiR trimers. Both the Li atoms and the R groups are arranged in an equilateral triangle.

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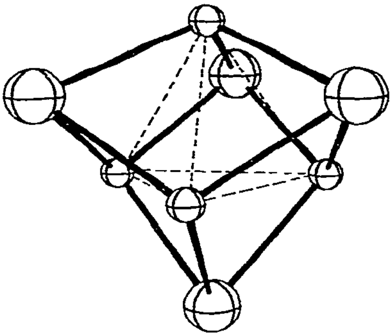
* This estimate was obtained by a "best fit" between the predictions of the theory and both our *ab initio* calculations and experimental results. The effective value of ε may be different when R is not methyl or ethyl.

** As suggested by a referee, nonbonded interactions between the R groups may also be a factor in limiting the number of neighbours. However, it should be pointed out that carbon–carbon distances of 3.5 and 3.6 Å (*i.e.* considerably shorter than twice the Van der Waals radius of 2.0 Å for a methyl group) are found in BLT[16] and ethyllithium[23] respectively.



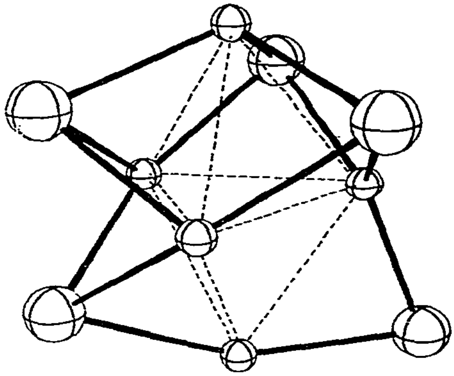


Fig. 4. Proposed structure for LiR tetramers. Both the Li atoms and the R groups are arranged in tetrahedrons.

Fig. 5. Proposed structure for LiR pentamers. Both the Li atoms and the R groups are arranged in a trigonal bipyramid.

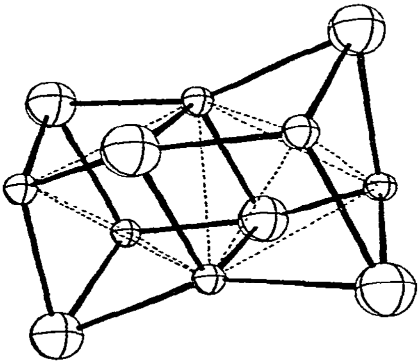


Fig. 6. Proposed structure for LiR hexamers. Both the Li atoms and the R groups are arranged as two tetrahedra having one common edge.

affected greatly reduces the energy binding of that R^- unit to the aggregate, and (*b*) excitation destroys *all* bonding interactions formed by a particular lithium–alkyl pair.

The optimum-energy geometrical structures predicted by the postulates for $(LiR)_n$ polymers for $n=2$ to 6 are illustrated* in Figs. 2–6; the positions of the Li^+ ions relative to each other and of the R^- ions relative to each other have been maximized to minimize the electrostatic repulsions. Per mole of LiR, the total bonding energy due to nearest-neighbour interactions is $2\,\varepsilon$ for the dimer, $2\frac{2}{3}\,\varepsilon$ for the trimer, 3ε for the tetramer, and $2\frac{4}{5}\varepsilon$ for the pentamer and $3\frac{1}{3}\varepsilon$ for the hexamer. Note first that the predicted dimerization energy of ≈ 34 kcal/mol agrees well with the *ab initio* value of 34.9, and that the predicted energy (per mole of LiR) to dissociate $(LiC_2H_5)_6$ of

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* The structures were drawn using the "ORTEP" computer program by C. K. Johnson (Oak Ridge Thermal-Ellipsoid Plot Program for Crystal Structure Illustration ORNL-3794) and supplied to us by Dr. N. C. Payne.

≈57 kcal/mol agrees well with the thermochemical value of 50.5. In addition, the prediction that aggregate stability should be in the order hexamer > tetramer > others (see Figs. 2–6) is in qualitative agreement with molecular weight studies[24] in solution for several alkyllithium systems (in which n is found to be either 4 or 6), and with the mass spectrometric studies[20] at 80–95° for gaseous methyllithium in which only the tetramer and hexamer were detected. Addition of a strong base to an alkyllithium solution is found to decrease n, but the coordination number never drops below 4.

The X-ray diffraction study[14] of the methyllithium tetramer confirms the prediction that the Li atoms are positioned in a tetrahedral orientation and similarly for the methyl groups. The theory also predicts that condensation of the aggregates should occur so as to produce additional nearest-neighbour $Li^+–R^-$ interactions; in the case of the tetramer and hexamer, one new bonding interaction* per mole of LiR should result when condensation occurs. The existence of short inter-aggregate Li–C distances (2.37 Å compared to 2.31 Å within the tetramer unit) in the crystal is in agreement with this prediction.

The predicted tetramerization energy of ≈51 kcal/mol per alkyl unit in $LiCH_3$ is substantially greater than that of 28.5 kcal/mol calculated *ab initio* by Guest *et al.*[3]. We feel that this latter value must be too small, given that hexamers exist in gaseous equilibrium with tetramers and that the experimental value for $(LiC_2H_5)_6$ is 50.5 kcal/mol. Part of the discrepancy here may arise from use of assumed geometries and orbital exponents in the GHS calculations; for example, their total energy for the $LiCH_3$ monomer is 57 kcal/mol less negative than that obtained in our calculations.

Postulate 3(b) leads to the rather unusual prediction that the $S_0 \rightarrow S_1$ excitation energy should increase with increasing size of the aggregate. In particular, the loss of bonding energy upon excitation of the dimer should be 2ε more than for the monomer, and should be 4ε greater than the monomer for the tetramer and hexamer. Assuming that the *ab initio* $S_0 \rightarrow S_1$ excitation energy for the $LiCH_3$ monomer of 82.0 kcal/mol is correct and holds also for LiC_2H_5, the corresponding transition in the dimer should require ≈116 kcal/mol (in good agreement with the *ab initio* prediction of 109.6), and ≈150 kcal/mol in both the methyl- and ethyl-lithium tetramers and hexamers [compared to 136 kcal/mol known for $(LiC_2H_5)_6$[21]]. The prediction that the excitation energies for the tetramer and hexamer should be virtually identical is supported by the recent assignments by Smart *et al.* of hexamer absorption at ≈133 kcal/mol for the ethyllithium hexamer and at ≈140 kcal/mol for the ethyllithium tetramer[25]. It is interesting to note that CNDO/2 calculations predict much too large (≈63 kcal/mol) a tetramer–hexamer splitting for this transition, which supports our comments above regarding the unreliability of semi-empirical calculations for these systems.

Finally, postulate 3(a) leads to the prediction that the residual bonding power of an alkyl group stripped of its extra electron via ionization should be very small, and therefore that the predominant ions in the mass spectrum of $(LiR)_n$ systems should be of the $(Li_nR_{n-1})^+$ type, in agreement with the peaks found in the mass spectrum of ethyllithium vapour[20].

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* The solid state structure in which the Li^+ units are oriented in an octahedral fashion (and similarly for the alkyl groups) cannot occur, since this would involve six nearest-neighbours for each Li^+, a number which exceeds the number of valence orbitals on lithium; see postulate 2.

In conclusion, the rather simple theory of bonding and energetics for alkyllithium aggregates proposed above is capable of *reproducing* in a semi-quantitative manner the known physical properties and *ab initio* calculations for such systems. Hopefully, further measurements and calculations will lead to refinements and elaboration of the postulates, particularly with regard to the variation in non-nearest neighbour interactions in the aggregates of different sizes. In particular, the effective Li–R energy in the monomer may well exceed the effective Li–R energy in the polymers, since the former does not include any amount due to Li^+–Li^+ and R^-–R^- interactions. On the other hand this difference in $E(Li^+–R^-)$ cannot be too great if the *ab initio* estimate of the dimerization energy is of the correct order of magnitude.

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