these nonchelated ligands with the remaining water molecules in the primary coordination sphere of the chelated lanthanide ion.[29,31]

As outlined above, a separation of the contact and pseudocontact components of each LIS by using the temperature-dependent data did not prove successful. The reasons for the failure in these systems vs. the excellent success in the exchange-inert Yb(DPA)$_3$ system[11] are not clear. Perhaps the line-width changes we observe in the chelated Ln(EDTA) resonances reflect a rather dramatic temperature-dependent structural change in this more flexible chelate. Such a structural change would clearly doom the temperature-dependent separation procedure to failure.

The temperature-independent Reilley method[17] not only proved useful for the separation of contact and pseudocontact shift components to the Ln(EDTA) but also provided indirect evidence for a Ln(EDTA) structural change near the center of the lanthanide series. Although the numerical values of G_i and F_i for the two Ln(EDTA) structural subgroups provide no specific structural information, we suspect that the change in G_i values near the center of the series parallels a decrease in coordination number perhaps due to the expulsion of one water molecule from the lanthanide coordination sphere. The minor changes in Ln–O and Ln–N bond lengths within each subgroup necessitated by decreasing cation size apparently do not preclude successful use of this separation method. Clearly, even the chelates within each subgroup are not "isostructural" but their dynamic solution structures are similar enough to allow evaluation of unique G_i and F_i values for the entire subgroup. The identical values of F_i for the two subgroups indicate that the structural change which increases G_i by nearly 50% does not alter the hyperfine coupling constant, A. Perhaps this is only fortuitous but we could argue that a structural alteration such as removal of one water molecule from the lanthanide coordination sphere would not necessarily change the lanthanide ion electron spin density reaching the carboxyl nucleus. Regardless, the constancy of A along the entire Ln(EDTA) series would have allowed a rapid estimation of the contact component to each shift by proportioning the shift observed for Gd(EDTA) to the relative $\langle S_z \rangle$ values for each lanthanide. This method of determining the contact component should, however, in general, be avoided for aqueous lanthanide species unless other evidence is available to indicate that A is relatively constant along the entire cation series.[5]

The positive electron spin density found at the carboxyl carbon nuclei in EDTA is similar to that measured in L-alanine at pH 3.[5] A comparison of the carboxyl contact shifts observed here with those of the exchange-inert trisdipicolinate chelates[11] shows that the latter are approximately 50% smaller than the EDTA shifts and the electron spin density at the carboxyl nuclei of dipicolinate is of opposite sign. This suggests that the unpaired spin density may be delocalized onto the carboxyl nuclei via a different mechanism in the aromatic chelate systems. Further chelate studies will be necessary to delineate such differences in electron delocalization mechanisms.

Acknowledgments. This research was supported in part by NIH Research Grant AM16947 from the National Institute of Arthritis, Metabolism, and Digestive Diseases, DHEW, and by Grant AT-584 from The Robert A. Welch Foundation. The Bruker WP-60 spectrometer was purchased in part by gifts from the Noble Research Foundation and The Lester Levy Family Fund.

Supplementary Material Available: Paramagnetic lanthanide-induced shifts in the carboxyl resonance of EDTA as a function of temperature (Table IV) (1 page). Ordering information is given on any current masthead page.

Electronic Structure of the Alkyllithium Clusters, $(CH_3Li)_n$, n = 1–6, and $(C_2H_5Li)_n$, n = 1–2

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Abstract: Optimized geometries and wave functions for the oligomers of CH_3Li, $(CH_3Li)_n$, for n = 1–6, and for the monomer and dimer of C_2H_5Li have been obtained by using the approximate molecular orbital method, PRDDO. Wave functions for $(CH_3Li)_n$, n = 1–3, have also been obtained from double-ζ basis sets. The properties of these oligomers have been examined by using both the canonical and localized molecular orbitals. Binding energies show that there exist stable planar arrangements of Li and C atoms for each oligomer n = 2–6 and that a condensed tetramer and condensed hexamer are also stable. The ionization potentials derived from Koopmans' theorem have been used to reinterpret experimental mass spectral studies. Bonding is discussed in terms of localized molecular orbitals obtained by using the Boys criteria. The bonding in these clusters is found to be multicentered involving closed three-center Li–C–Li and closed four-centered Li_3C bonds. The ethyllithium compounds are found to be very similar to their methyl counterparts.

Introduction

Currently there is wide interest in molecules containing lithium and organic fragments.[2a–d] This interest is due to their use as synthetic reagents[2e] and to their novel bonding and spin properties.[3] These molecules are also useful as models for simple electron-deficient metal clusters, an added advantage being that they have been partially characterized experimentally. Since they are electron deficient, these compounds can oligomerize and should form multicentered bonds that are analogous to bonding patterns found in the boron hydrides and carbonanes.[4] Oligomers of the

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Table I. Geometric Parameters for the $(CH_3Li)_n$ Oligomers

n	geometry[a]	r(LiLi)[b]	r(CC)[b]	r(LiC)[b]	θ(LiCLi)[c]	θ(CLiC)[c]	θ(HCH)[c]
1[d]	C_{3v}			1.98			106.4
2[d]	D_{2h}	2.06	3.72	2.13	57.9	122.1	104.8
3[d]	D_{3h}	2.36	4.04	2.03	71.1	168.9	103.4
4[d]	D_{4h}	2.53	4.06	2.04	76.5	166.8	104.0
4[d]	T_d	2.18	3.46	2.09	62.6	111.5	102.9
5[e]	D_{5h}	2.53	3.93	2.04	76.6	148.6	104.0
5[f]	C_s	2.38	2.18	2.20	65.5	109.8	105.0
6[e]	D_{6h}	2.53	3.79	2.04	76.6	136.6	104.0
6[f]	D_{3d}	2.20	3.79	2.09	63.8	122.2	108.3

[a] Conformations shown in Figure 1. [b] Bond lengths in angstroms. [c] Bond angles in degrees. [d] Geometry optimized. [e] Parameters from $(LiCH_3)_4$ D_{4h} calculation. [f] Partial geometry optimization.

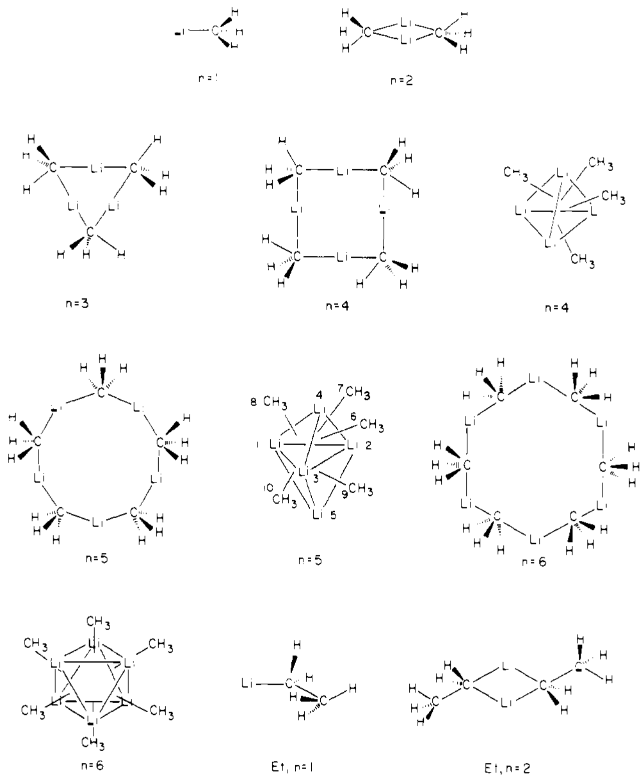

Figure 1. Geometries employed for the various $(LiCH_3)_n$ clusters and for LiC_2H_5 and $(LiC_2H_5)_2$. Note for n = 4, 5, and 6 that two forms, planar and condensed, are considered. Coordinates are given in the Appendix.

form $(LiR)_n$ where R is an alkyl group have been observed in the gas phase,[5] in solution,[6] and in the solid state.[7] The crystal structure as determined by X-ray diffraction for CH_3Li[7a,b] shows a distinct tetrahedral tetrameric unit while the crystal structure for C_2H_5Li[7c] shows a distorted tetrahedral tetramer. Crystal structures of π-complexed lithium systems have also been reported.[7e,f] Mass-spectral studies[5a] of ethyllithium vapor reveal the existence of hexamers and tetramers in the gas phase while solution studies on alkyllithiums[6] show that hexamers and tetramers can be present. It has been suggested that larger alkyl groups correspond to lower degrees of association in solution.[8]

There is, at present, one ab initio calculation on the $(CH_3Li)_2$ dimer[9] and one on the $(CH_3Li)_4$ tetramer.[10] However, full geometry optimization was not carried out for these molecules and general trends could not be elucidated by a comparison of the two studies. A number of ab initio calculations of $(LiH)_n$ clusters for n = 1-6 have been performed at least at the double-ζ level.[11-13] These studies have determined stable geometries, and studies on the dimer have shown that correlation effects are not important in determining binding energies in these compounds. For calculations on larger LiH clusters such as $(LiH)_{16}$ or on $(CH_3Li)_6$, ab initio calculations are presently not feasible owing to computational costs. However, one can employ approximate methods which are computationally very efficient for such studies. The approximate method PRDDO[14,15] (partial retention of diatomic differential overlap) includes all electrons in a minimum basis set of Slater orbitals, and has been found to yield results that are in good agreement with those from ab initio minimum basis set calculations, using either the STO-3G expansion[16] or Slater orbitals. However, PRDDO requires only 6% of the computational time necessary for an STO-3G calculation, using the program GAUSSIAN-70.[17] In our studies[13] on the $(LiH)_n$ polymers, reasonable agreement between the PRDDO and the ab intio calculations was found for both the geometry and dissociation energy of the cluster to monomers. We have thus employed the computationally efficient PRDDO method for most of our studies on the alkyllithium clusters.

We present PRDDO calculations on the $(CH_3LI)_n$ clusters in various geometries for n = 1-6 and on the monomer and dimer of C_2H_5Li. The structures for these molecules are shown in Figure 1. For convenience, the symmetries (Table I) that are used below are given for the cluster ignoring the methyl hydrogens. Thus, we have labeled the point groups of the molecules based on the point group of the lithium-carbon skeleton rather than the full molecular point group, e.g.,D_{nh} instead of C_{nh}. The electronic structures of these molecules are described in terms of the atomic charges, canonical molecular orbitals (CMO), and CMO eigenvalues. Bonding in these oligomers is described in a localized molecular orbital (LMO) framework where the LMOs were calculated by using the Boys criteria.[18,19] We also present ab initio calculations on $(CH_3Li)_n$, n = 1-3, using both STO-3G and

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Table II. Geometric Parameters for Monomers and Dimers of C_2H_5Li

n	$R(\mathrm{LiLi})^a$	$R(\mathrm{CC})^a$	$R(\mathrm{LiC})^a$	$R(\mathrm{CC'})^a$	$\theta(\mathrm{LiCLi})^b$	$\theta(\mathrm{CLiC})^b$
1^c			2.03	1.51		
2^d	1.98	3.72	2.11	1.51	56.0	124.0

[a] Bond lengths in angstroms. [b] Bond angles in degrees. [c] Geometry optimized. [d] Li_2C_2 core geometry optimized. Remaining parameters from monomer geometry.

Table III. PRDDO Binding Energies and Ionization Potentials for $(CH_3Li)_n$

n	geometry	BE/monomer[a]	IP[b]	total energy[c]
1	C_{3v}		7.42	−46.929 37
2	D_{2h}	18.0	7.83	−93.915 98
3	D_{3h}	26.3	8.87	−140.913 88
4	D_{4h}	28.6	9.04	−187.899 93
4	T_d	27.1	8.72	−187.890 16
5	D_{5h}	28.6	9.06	−234.874 37
5	C_s	11.6	6.27	−234.739 08
6	D_{6h}	27.8	9.09	−281.842 15
6	D_{3d}	23.0	7.61	−281.796 29

[a] Binding energy/monomer in kcal/mol. BE/monomer = $\{E[(CH_3Li)_n] - nE(CH_3Li)\}/n$. [b] Ionization potential determined from Koopmans' theorem in eV. [c] Energy given in atomic units (1 au = 627.5 kcal/mol).

Table IV. Ab Initio Total Energies, Binding Energies, and Ionization Potentials for $(CH_3Li)_n$, $n = 1$–3

n	basis set	SCF energy[a]	BE/monomer[b]	IP[c]
1	STO-3G[d]	−46.418 74		6.45
2	STO-3G[d]	−92.896 88	18.6	6.88
3	STO-3G[d]	−139.382 30	26.4	7.84
1	DZ[e]	−46.986 78		7.42
2	DZ[e]	−94.036 76	19.8	8.33
3	DZ[e]	−141.078 53	24.7	9.25

[a] Total SCF energy in atomic units (1 au = 627.5 kcal/mol). [b] Binding energy/monomer in kcal/mol. [c] Ionization potential from Koopmans' theorem in eV. [d] Minimum basis set. [e] Double ζ basis set.

Table V. PRDDO Total Energies, Binding Energies, and Ionization Potentials for the Monomer and Dimer of LiC_2H_5

n	SCF energy[a]	BE/monomer[b]	IP[c]
1	−85.918 56		6.81
2	−171.892 23	17.2	7.26

[a] Total SCF energy in atomic units. [b] Binding energy/monomer in kcal/mol. [c] Ionization potential from Koopmans' theorem in eV.

double ζ basis sets. These calculations were carried out to show that the PRDDO results were giving reasonable predictions.

Calculations

The exponents of the STO basis sets for these molecules are taken from the work of Pople et al.[16] (Li(1s) = 2.69, Li(2s) = Li(2p) = 0.80, C(1s) = 5.67, C(2s) = C(2p) = 1.72) except for the hydrogen exponents, which were set to the value of 1.2. The geometries for the polymers $(CH_3Li)_n$, $n = 1$–4, were optimized constrained to the structures given in Figure 1 and subject to the additional constraint that the methyl groups have a local C_{3v} axis. These geometries were chosen based on previous calculations[12,13] on $(LiH)_n$ clusters, which should have similar stable forms. All remaining parameters were varied except for the C-H bond lengths in the D_{3h} and D_{4h} molecules, which were set at 1.07 Å following the results found for the dimer. For $n = 2$ and 3 the planar clusters had one hydrogen in the plane containing the lithiums and carbons, while for $n = 4$, 5, and 6 there were no hydrogens coplanar with the heavy atoms. The geometry for C_2H_5Li was fully optimized and the carbon–lithium core of the dimer $(C_2H_5Li)_2$ was also optimized with the remaining parameters taken from the monomer structure. A number of calculations were carried out on the pentamer and hexamer of methyllithium with geometry parameters taken from various tetramer results. Because of the computational expense even at the PRDDO level, full geometry optimization of these structures could not be performed. The geometries of the planar pentamer and hexamer were generated by using the Li–Li and Li–C bond lengths and the geometry of the methyl group found for the D_{4h} tetramer. The geometries of the more highly condensed structures, the C_s pentamer and D_{3d} hexamer were initially calculated with parameters from the T_d tetramer structure. The Li–Li and Li–C distances in these condensed structures were then partially optimized. For the D_{3d} geometry, a calculation was also performed at the Li–Li distance from D_{3d} $(LiH)_6$[13] with a reasonable Li–C distance, but this gave a much higher energy.

The ab initio calculations using both the STO-3G and double ζ (DZ) basis sets were carried out with the HONDO version 3 program.[20] The DZ basis sets were of the form (95)/[32] on Li and C and (4)/[2] on H with exponents and contraction coefficients taken from Dunning and Hay.[21] The Li–C and H–C–H angle θ for CH_3Li were optimized by using the DZ basis yielding $R(\mathrm{Li{-}C}) = 2.02$ Å and $\theta = 107°$. The value for Li–C bond length was used to scale the optimized PRDDO geometries for the dimer and trimer in order to obtain geometries for the STO-3G and DZ calculations.

The localized molecular orbitals were calculated by using the Boys criteria[19] following the Edmiston–Ruedenberg procedure.[22] The implementation of the method has been discussed previously.[19]

Results.

Structure and Energetics. The important molecular parameters of the methyllithium oligomer structures obtained from the PRDDO optimizations are given in Table I, where they are compared to other calculations and to experiment. The geometry results for the ethyl-substituted compounds are given in Table II. The atomic Cartesian coordinates for the molecules studied are given in a supplementary appendix. The PRDDO total energies for the CH_3Li oligomers are reported in Table III, as are the binding energies per monomer unit given together with the ionization potentials as determined from Koopmans' theorem.[23] The ab initio energy results are summarized in Table IV while the PRDDO results for the ethyllithium compounds are given in Table V.

The theoretical bond distances for the C–Li bond in CH_3Li are all close to 2.0 Å with PRDDO showing a tendency to slightly underestimate this bond length as compared to the ab initio calculations. The parameters for the dimer are somewhat shorter than those used in the previous STO-2G calculations,[9] but our geometry is significantly more accurate as a full geometry optimization was performed. Using our comparison between the PRDDO and DZ calculations on $(LiH)_n$ clusters, it is likely that our PRDDO bond distances are somewhat short. It is interesting to note that the bond distance for the C–Li bond in the dimer does not show a large change from that found for the monomer. We also find that the rotation barrier (0.4 kcal/mol) for a CH_3 group in the dimer is negligible. The D_{3h} planar trimer exhibits a lengthening of the Li–Li bond and a decrease of the Li–C bond length as compared to the dimer that gives a value for $R(\mathrm{Li{-}C})$ near that found for the monomer. The planar tetramer again shows an increase in the Li–Li distance, but very little change in the Li–C distance is observed. The rotation barrier for the

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methyl group in the trimer is also small at 0.5 kcal/mol. For the planar tetramer, only 1.8 kcal/mol is required to rotate all of the methyls simultaneously. The Li–C distance of the tetrahedral tetramer increases slightly from that found for the D_{4h} isomer, but the Li–Li distance shows a dramatic shortening. Comparison with the crystal structure[7a] shows that all of the bond distances for PRDDO are significantly shorter than those found by crystallographic methods. However, the Li–C distances between two different tetramers in the crystal are comparable to Li–C distances within a tetrameric unit, suggesting the possibility of an infinite order type structure rather than discrete tetramers. This could account for some of the observed differences in the bond lengths as the crystal may not correspond to discrete tetrameric units. These distances would not be appropriate to compare to those of our structure, which is relevant to an isolated gas-phase cluster. In agreement with the crystal structure, the PRDDO calculations do predict shorter Li–C bond lengths as compared to the Li–Li bonds. The rotation barrier for one methyl group in the tetramer is 4.4 kcal/mol with the constraint that the remainder of the geometry is held constant. This barrier is somewhat larger than found in the planar structures, suggesting that there are larger steric interactions in this condensed arrangement. The geometries for the planar trimer of CH_3Li and higher planar clusters show increasing Li–Li distances relative to the corresponding distance in the dimer. This can be attributed to the fact that there is only one bridging methyl group for these molecules while there are two bridging methyl groups in the dimer. In agreement with this simple argument, we find that the more highly condensed structures that have multicentered bonds to the methyl bridges have shorter Li–Li bond lengths than found in the corresponding planar structure, but still have longer Li–Li bond lengths than found for the dimer.

The bond lengths in the ethyl molecules show interesting trends. The Li–C bond length in the C_2H_5Li monomer is longer than that found in CH_3Li while the Li–C bond length in $(C_2H_5Li)_2$ is somewhat shorter than found in $(CH_3Li)_2$. The Li–Li distance also shrinks somewhat in $(C_2H_5Li)_2$ as compared to the Ch_2H_5Li monomer value. We note that for both dimers the Li–Li distance is significantly *shorter* than that found for Li_2, where the bond length is 2.68 Å.[23]

The variation in H–C–H angles for various clusters is also quite interesting. The H–C–H angle in CH_3Li is 106.4°, decreasing to 104.8° in the dimer and 103.7° in the trimer. In the D_{4h} isomer of the tetramer the angle is 104.0°, while for the T_d tetramer the angle is decreased to 102.9°. This general trend of decreasing bond angle is similar to the results found by Collins et al.,[24] who predict that bonding patterns approaching in the limit a planar carbon would be expected with an increase in the electron-deficient nature of the bonds to the carbon atom. The H–C–H bond angle in ethyllithium shows a greater decrease (103.9°) than found for Ch_3Li and the C′–C–Li bond angle is quite large (118.1°). However, the C′–C–H angles are very nearly tetrahedral (109.2°) as are the H–C–Li angles (107.7°).

Molecular dipole moments have been calculated for the monomers giving $\mu(CH_3Li) = 4.60$ and $\mu(C_2H_5Li) = 4.70$ D.

The most important quantity in describing the binding energies of these clusters is their dissociation energy to the various monomer units. In Table III we present the PRDDO results for the dissociation energy to monomers for the CH_3Li clusters. The quantity is given as the stability energy per monomer unit in order to facilitate comparison between clusters of different sizes. The dimerization energy of CH_3Li to form $(CH_3Li)_2$ is −36.0 kcal/mol or 18 kcal/mol of stabilization energy/CH_3Li monomer unit. The planar trimer shows a significantly enhanced stability over that of the dimer even though the Li–Li bridging is accomplished with only one methyl group. The remaining planar clusters for n = 4, 5, and 6 have very similar stabilization energies with the D_{4h} isomer being over 2 kcal/mol per monomer unit more stable than the D_{3h} isomer. A slight drop is noted in going from the D_{5h} to the D_{6h} cluster but this could be due to our use of assumed rather than fully optimized geometries.

In order to ensure that our PRDDO results give reasonable predictions, we have performed STO-3G and DZ calculations on the monomer, dimer, and trimer of CH_3Li. (The STO-3G results were required as starting points for the DZ calculations in order to achieve SCF convergence.) The STO-3G results are essentially identical with the PRDDO results. The DZ calculations are also in excellent agreement with the minimum basis set results with the dimer showing a slightly greater binding energy and the trimer showing a slight decrease relative to the PRDDO values. This latter variation could easily be due to the fact that the geometries employed in the DZ calculations were not optimal for this basis set. Previous calculations[12] on $(LiH)_n$ have shown that correlation effects are not important in determining the binding energies of these clusters and we expect a similar lack of correlation corrections to the binding energies for the CH_3Li molecules. Thus, our PRDDO values should provide a reasonable description of the energetics of the alkyllithium clusters.

We now compare the energies of the more highly condensed oligomers with the planar structures. For the tetramer we considered both the tetrahedral and planar forms. The D_{4h} structure is slightly more stable than the T_d isomer, but the difference is small, and thus we cannot unequivocally predict the preferred configuration. The effect of correlation corrections[12] in the $(LiH)_4$ compounds favors the T_d structure over the D_{4h} by 4 kcal/mol. This is most likely due to the increased multicentered bonding in the T_d isomer as compared to the D_{4h} form. This same correlation effect should be present in the CH_3Li clusters and this suggests that the T_d structure could be more stable. Comparison of the results for the pentameric oligomers shows that a C_s condensed structure based on a trigonal-bipyramidal arrangement of Li atoms with a vacant triangular face is quite unstable relative to the D_{5h} planar form. However, this C_s structure is still bound with respect to dissociation to monomers. Since a partial geometry optimization was carried out, it is unlikely that the 80 kcal/mol difference between the C_s and D_{5h} isomers will be completely made up by further geometry optimization. The instability of the C_s structure could be due to a steric crowding of the methyl groups that requires a lengthening of the Li–C bond. In contrast to the results observed for the pentamer, the condensed D_{3d} and planar D_{6h} structures of the hexamer have similar energies, although the D_{6h} form is more stable by ~5 kcal/mol per monomer. Further geometry optimization would lower this difference somewhat, but probably would not account for all of it. In comparison to the C_s structure of the pentamer, the D_{3d} structure probably shows much less crowding of the methyl groups, thereby decreasing the steric problem. As discussed later, the LMO bonding pattern for the D_{3d} structure suggests that this molecule can be considered as two weakly interacting D_{3h} $(CH_3Li)_3$ groups. Thus, correlation effects should be smaller here than in the T_d structure as less multicentered bonding is present.

We now compare our results for the CH_3Li oligomers to those obtained in previous studies. The dimerization energy obtained from the STO-3G calculation of Baird et al.[9] is 17.5 kcal/mol per monomer as compared to our STO-3G value of 18.6 kcal/mol, which shows that our geometry is somewhat better. However, the small energy difference found between calculations based on significantly different atomic coordinates does show that the molecule is quite floppy. The binding energy for the T_d tetramer obtained by Guest et al.,[10] using a minimum basis set, is 28.5 kcal/mol per monomer, in comparison with our value of 27.1 kcal/mol per monomer. These results are in reasonable agreement, considering the difference in basis sets. Further comparison with their result is not possible as no information on the geometry was provided. Our results suggest that the ionic model for bonding and energetics in the alkyllithiums proposed by Baird et al.[9] is too simplistic. This is true both for the predictions of geometry and for the energetics of aggregation. Our results support the energetics found by Guest et al.[10] for the T_d tetramer rather than the conclusions of Baird et al.,[9] who significantly overestimate the binding energy.

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(24) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. von R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976).

Table VI. Charge Distribution[a] in the Highest Occupied Molecular Orbital (HOMO) of $(CH_3Li)_n$

n	geometry	orbital degeneracy	Li(2s)	Li(2p)	C(2s)	C(2p)
1	C_{3v}	1	0.40	0.31	0.05	1.13
2	D_{2h}	1	0.00	0.25	0.04	0.64
3	D_{3h}[b]	2	0.07	0.29	0.04	0.83
4	D_{4h}[b]	2	0.11	0.21	0.03	0.59
4	T_d[b]	3	0.05	0.27	0.07	0.93
5	D_{5h}[b]	2	0.11	0.15	0.03	0.47
6	D_{6h}[b]	2	0.12	0.11	0.02	0.37
6	D_{3d}	1	0.04	0.06	0.01	0.20
5	C_s	1	0.00 (1,3)[c]	0.08	0.04 (6,7)[c]	0.41
			0.00 (4,5)[c]	0.10	0.03 (9,10)[c]	0.25

[a] Given in units of electron. [b] These orbital populations obtained by summing the population in the degenerate orbitals. [c] Atom numbers shown in Figure 1. Li(2) and C(8) do not participate in the HOMO.

Table VII. Analysis of Charge Distributions for the Monomer and Dimer of C_2H_5Li

A. HOMO Charge Distribution[a]

n	orbital degeneracy	Li(2s)	Li(2p)	C(2s)[b]	C(2p)[b]
1	1	0.40	0.29	0.04	1.00
2	1	0.00	0.23	0.03	0.60

B. Charge Distribution[a]

n	Li	C[b]	Li(2s)	Li(2pσ)[c]	Li(2pπ)[d]
1	0.19	−0.15	0.45	0.35	0.03
2	0.21	−0.20	0.32	0.46	0.02

[a] Units of electrons. [b] We include only the carbons adjacent to lithiums. [c] In-plane p orbitals. [d] Out-of-plane p orbitals.

The ethyllithium dimer has a dimerization energy of 16.6 kcal/mol in reasonable agreement with the value for the methyllithium dimer.

We now briefly compare our results on the alkyllithiums to those obtained for $(LiH)_n$ clusters.[13] The LiH clusters show a higher bonding energy/monomer than do the corresponding CH_3Li clusters. This is due, in part, to a reduction of steric hindrances in the LiH aggregates. The Li-Li bond distances are also somewhat longer in the LiH dimers. The same pattern of bonding energies is followed for both types of clusters. For $(LiH)_n$, there is a large gap between the dimer and trimer energies, although the binding energies per LiH unit of the planar clusters up to $n = 16$ are quite similar. The T_d and D_{4h} tetramers of LiH are of comparable energy as are the D_{6h} and D_{3d} hexamers, the D_{3d} being slightly favored. As we found for $(LiCH_3)_5$, the C_s structure for $(LiH)_5$ is very unstable as compared to the D_{5h} form.

From data obtained in solution NMR studies, Brown[5b,25] suggests that $(LiR)_4$ dissociates into $2(LiR)_2$, although the direct process was not observed. From their measurements they suggest that this process occurs with activation energies of 11[25b] and 24 kcal/mol[5b] for R = ethyl and R = *tert*-butyl, respectively. From our calculated binding energies, this explanation seems unlikely unless solvation is extremely important since dissociation of $(LiCH_3)_4$ to $2(LiCH_3)_2$ would require 43 kcal/mol. It is possible that the NMR results could be explained by a rearrangement between the two isomeric forms of the tetramer. Finally, we note that Wittig[26] has postulated to the existence of $(LiCH_3)_3$ to account for ebulliometry measurements of methyllithium in boiling ether.

Canonical Molecular Orbitals. The ionization potentials (IP) determined, using Koopmans' theorem for the methyllithiums show interesting trends. The IP for the dimer is higher than that of the monomer as are, in general, all of the ionization potentials. The IPs obtained from the STO-3G and DZ calculations show different absolute values, but exhibit the same trend as found for the PRDDO calculations, i.e., an increase in IP as size increases for the planar molecules. The planar structures tend to have higher IPs than do the more condensed forms. A difference of almost 3 eV is predicted between the IP of the D_{5h} and C_s pentamers, with the less stable structure having the lower IP. A difference of 1.5 eV in IP is noted between the D_{3d} and D_{6h} forms of the hexamer while a difference of only 0.3 eV is noted between the two forms of the tetramer.

The ionization potentials for the ethyllithium monomer and dimer behave in a similar fashion to the monomer and dimer of methyllithium; the dimer shows a higher IP than found for the monomer. The effect of the additional methyl substituent on each is to lower the IPs of the ethyllithium compounds relative to the corresponding methyllithium oligomers.

The actual location of the highest occupied molecular orbital (HOMO) is important in determining mass spectrometric fragmentation patterns for the alkyllithium oligomers (see Table VI for the CH_3Li compounds). In CH_3Li, the HOMO is localized in the Li–C bond with more density on C than on Li, in agreement with the LMO description given below. The HOMO in the dimer is localized in the in-plane $2p_y$ orbitals for both Li and C where Y is aligned on the Li–Li axis. In this HOMO, each Li has 0.25 e while each C has 0.64 e; thus, the electrons are more localized on C. The HOMO for the trimer is doubly dengenerate and we have summed the atomic orbital populations in the two molecular orbitals for our analysis. These results show, again, that there is significantly more density on C than on Li. We do see some evidence of Li(2s) character in the HOMO. For the larger compounds we find a general trend of increasing Li(2s) character and a modest decrease of C(2p) character in the HOMO. The dominant portion of the density remains on the carbon. The results for the ethyllithium monomer and dimer are in agreement with these generalizations (Table VII).

Mass-spectral studies of the ethyllithium clusters[5] show that loss of an ethyl group is the predominant feature in the spectrum; little or no parent is observed. This result is in agreement with our observation that the HOMO electrons are predominantly localized on carbon rather than on the lithiums. These experimental studies[5] show that the appearance potentials for the formation of $Li_6R_5^+$ and $Li_4R_3^+$ are significantly lower than the corresponding potentials for formation of $Li_5R_4^+$, $Li_3R_2^+$, and Li_2R^+ for R = ethyl. These results were interpreted as showing that only the hexamer and tetramer are in equilibrium in the gas phase. This explanation is in disagreement with our calculations that show that the oligomers of CH_3Li have very similar binding energies for $n = 3$–6. The interpretation of the experiments assumes that the process $Li_nR_n + e^- \rightarrow Li_nR_{n-1}^+ + R + 2e^-$ will yield ions of similar stabilities and that the neutral oligomers all have similar ionization potentials. However, our results show that the IPs for the condensed and planar structures are different, with the IPs for the planar structure being larger. It is also likely that the planar molecules will lose R groups less efficiently than loss from a condensed structure because more rearrangement probably occurs in the $Li_nR_{n-1}^+$ ion derived from the planar isomer. Our theoretical results would then suggest quite a different interpretation of these experiments than that previously given. Our interpretation is that the peaks $Li_nR_{n-1}^+$ in the mass spectrum actually correspond at low electron energies to loss of R from a parent neutral Li_nR_n rather than from fragmentation of the tetramer and hexamer. The variation in appearance potentials is due both to the variations in IP because of differences in geometry and to the different mechanisms by which R is lost from a given cluster. A cautionary note to our interpretation must be given. If the relative energies of the various sizes of clusters differ by 3–5 kcal/mol (which is within the error limits of our calculations), then certain clusters could easily be present at <1% abundance in the equilibrium vapor. Such small amounts would be difficult to observe in the mass spectrum, especially near threshold regions.

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(25) (a) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966); (b) K. C. Williams and T. L. Brown, *ibid.*, **88**, 4134 (1966).

(26) G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **57**, 167 (1951).

Table VIII. Atomic Charges[a] for $(CH_3Li)_n$ Oligomers and Orbital Analysis of Li Charge

n	geometry	Li	C	Li(2s)	Li-(2pσ)[b]	Li-(2pπ)[c]
1	C_{3v}	0.21	−0.23	0.43	0.32	0.03
2	D_{2h}	0.23	−0.27	0.32	0.44	0.02
3	D_{3h}	0.20	−0.28	0.35	0.43	0.03
4	D_{4h}	0.17	−0.27	0.35	0.46	0.03
4	T_d	0.25	−0.31	0.35	0.42[d]	
5	D_{5h}	0.14	−0.27	0.35	0.48	0.03
6	D_{6h}	0.13	−0.27	0.35	0.50	0.03
6	D_{3d}	0.15	−0.23	0.42	0.44[d]	
5[e]	C_s	0.17 (1,3)	−0.25 (6,7)	0.37	0.47[d]	
		0.29 (2)	−0.28 (8)	0.32	0.42[d]	
		0.23 (4)	−0.23 (9,10)	0.32	0.47[d]	
		0.17 (5)		0.39	0.45[d]	

[a] Units of electrons. [b] In-plane p orbitals. [c] Out-of-plane p orbitals. [d] For condensed structures we report the total amount of p character. [e] Numbering scheme given in Figure 1.

Table IX. Overlap Populations for $(CH_3Li)_n$

n	geometry	Li-C	Li-Li
1	C_{3v}	0.618	
2	D_{2h}	0.329	0.279
3	D_{3h}	0.349	0.129
4	D_{4h}	0.331	0.193
4	T_d	0.276	−0.039
5	D_{5h}	0.328	0.189
6	D_{6h}	0.328	0.182
6	D_{3d}	0.315[a]	0.040
		0.194[b]	
5	C_s[c]	0.290 (1-7)	0.119 (1-4)
		0.246 (1-10)	
		0.223 (2-6)	0.087 (2-4)
		0.113 (2-9)	0.070 (2-5)
		0.263 (4-6)	
		0.178 (4-8)	
		0.356 (5-9)	

[a] Overlap of one of two equivalent lithiums. [b] Overlap to unique lithium in the face. [c] See Figure 1 for numbering scheme. Only unique values are given.

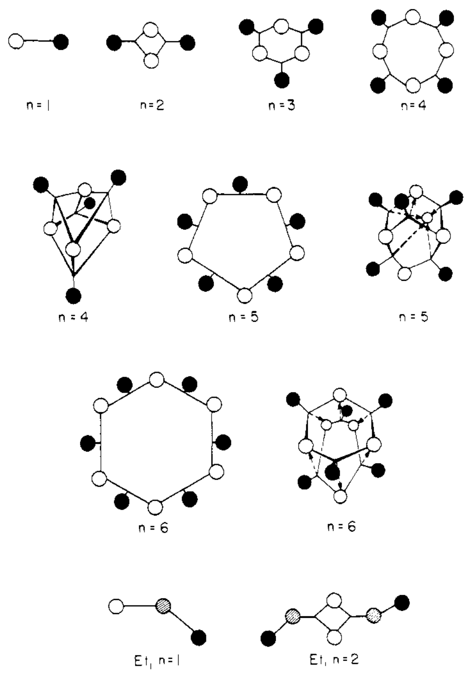

Figure 2. Framework localized molecular oribitals for the various clusters. Only bonds between Li and C are shown; no C–H bonds are given. Open circles are Li atoms, dark circles are C atoms in CH_3 groups, and shaded circles are C atoms in the CH_2 groups of ethyllithium complexes. Solid lines denote normal participation in multicentered bonds and dashed arrows show weak atomic donation (0.15–0.25 e) to a multicentered bond. Note the fractional center in the condensed structure for $n = 5$.

The canonical molecular orbitals can also be used to obtain molecular charges and overlap populations that are useful in understanding the bonding in these complex systems. For simplicity and to avoid some of the problems of the Mulliken population analysis, we compare a CH_3 group charge for the methyllithiums instead of a carbon charge. Since the positive charges on H are small, the interpretation would not vary significantly even if we were to examine only atomic charges. Thus the CH_3 group charge is just the negative of the Li charge given in Table VIII. For $(LiCH_3)_n$, $n = 1–3$, the Li has charge of ∼+0.2 e. As the size of the planar cluster increases the charge on Li shows a monotonic decrease. The T_d tetramer has a larger charge on lithium than any other cluster, implying that there is more ionic character in this complex. The D_{3d} hexamer shows a much smaller charge separation than does the T_d tetramer, although the Li charge on the D_{3d} hexamer is somewhat larger than was found for the D_{6h} structure. As expected the ethyllithium clusters follow a pattern similar to that found for the CH_3Li monomer and dimer.

We have reported the populations on the lithiums in terms of the contributions of the 2s, 2pσ, and 2pπ orbitals for the planar structures and 2s and 2p for the condensed structures in Table VIII. In CH_3Li there is more 2s than 2pσ character in the Li–C bond with very little 2pπ character. In the larger planar clusters there is more 2pσ character than 2s character in the bonds and there is very little 2π out-of-plane bonding. In the condensed structures there is more 2p than 2s character with the exception that there is little difference between the 2s and 2p populations for the D_{3d} hexamer.

Overlap populations are useful in examining whether there is a significant interaction between the lithiums in a cluster. These are summarized in Table IX for the CH_3Li oligomers. The Li–C bond overlap as compared to that found for CH_3Li decreases significantly as soon as clusters are formed. For the dimer a significant amount of Li–Li overlap is seen. The trimer shows a large decrease relative to the dimer while the planar tetramer has a larger overlap than is found for the trimer. The planar pentamer and hexamer have Li–Li overlaps that are similar to those found for the D_{4h} tetramer. The Li–C overlap populations for these larger oligomers remain essentially the same as those of the dimer. Thus, all of the planar structures show a significant amount of metal–metal bonding. In contrast the T_d tetramer shows essentially no metal–metal bonding as all of the bonding occurs via the bridging methyl groups; the lithium orbitals are directed exo to the occupied triangular faces. The D_{3d} hexamer shows a small amount of metal–metal bonding between lithiums in an occupied triangular face. The overlap populations show that the bonding of the methyls is greater to the two lithiums that are adjacent to the vacant triangular face than it is to the remaining lithium. This aspect of the bonding in the D_{3d} hexamer is discussed in greater detail below in terms of LMOs. There have been a number of suggestions[2b] about the extent of metal–metal bonding in these systems. Based on the above results, we expect significant metal–metal bonding in the planar forms, but very little in the clusters. We have also investigated the possibility that Li–H interactions from hydrogens on the CH_3 are important.[27] In the planar forms, such interactions are not significant as the Li–H overlaps are small. However, the Li–H overlap populations in the T_d tetramer and D_{3d} hexamer are much larger, suggesting some interaction between Li and H. We note that this difference in Li–H overlap between the planar and condensed forms occurs even though the Li–H distances are quite similar.

Localized Molecular Orbitals. The simplified orbital diagrams derived from the localized molecular orbital analysis are shown in Figure 2. A detailed analysis of the orbitals for the CH_3Li cluster is given in Table X while the results for C_2H_5Li and

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[27] (a) I. Craubner, *Z. Phys. Chem.* (*Frankfurt am Main*), **51**, 225 (1966); (b) R. P. Zerger, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **96**, 6048 (1974).

Table X. Analysis of Localized Molecular Orbitals between Li and C for the $(CH_3Li)_n$ Oligomers for $n = 1$-6

n	geometry	pop(Li)[a,b]	pop(C)[a]	sp^x(Li)[c]	sp^x(C)[c]	θ(C-Li-cc)[d]	θ(Li-C-cc)[d]
1	C_{3v}	0.83	1.22	0.7	4.0		
2	D_{2h}	0.37	1.29	1.9	3.4	3	29
3	D_{3h}	0.40	1.28	1.5	3.6	22	36
4	D_{4h}	0.40	1.24	1.5	3.6	24	38
4	T_d[e]	0.24	1.38	1.7	2.9		
5	D_{5h}	0.41	1.22	1.7	3.6	25	38
6	D_{6h}	0.41	1.21	1.9	3.6	25	38
6	D_{3d}	0.33	1.32	1.0	3.7	38	37

LMOs for C_s $(CH_3Li)_5$

bond[f]	pop(Li)	pop(C)	pop(Li)	sp^x(Li)	sp^x(C)	sp^x(Li)	θ(C-Li-cc)	θ(Li-C-cc)	θ(C-Li-cc)
3-8-1	0.29	1.25	0.29	1.0	3.2	1.0	30	38	30
3-9-5[g]	0.28	1.21	0.39	1.6	3.0	1.2	38	33, 27	38
1-7-4[h]	0.28	1.27	0.25	1.5	2.8	2.2	13	0, 0	13

[a] Population in electrons (e). [b] There are two equivalent Li atoms in each Li-C-Li three-centered bond. [c] Hybridization. The value of x is given. [d] Angles to centroid-of-charge (cc) in degrees. [e] For this structure there are three equivalent Li atoms in each four-centered bond. [f] Numbering as in Figure 1. Each value given in the order of the bond numbering scheme. [g] This is equivalent to the 5-10-1 bond. [h] This is equivalent to the 3-8-4 bond.

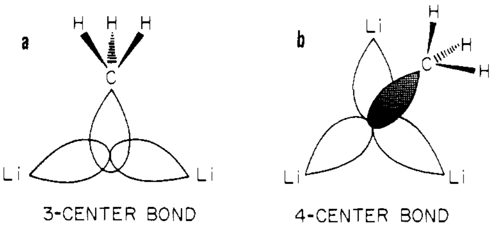
Table XI. Analysis of Localized Molecular Orbitals between Li and C for the Monomer and Dimer of C_2H_5Li[a]

n	pop(Li)	pop(C)	sp^x(Li)	sp^x(C)	θ(C-Li-cc)	θ(Li-C-cc)
1	0.86	1.18	0.7	4.2	8	4
2	0.38	1.28	1.7	4.0	29	7

[a] See Table X for description.

$(C_2H_5Li)_2$ are shown in Table XI. The methyllithium structure corresponds to the simple valence bond scheme expected for this molecule. The hydbridization at C for the polar Li-C bond is sp^4 with a hybridization on Li of $sp^{0.7}$, showing the large amount of Li(2s) character in this bond. The C-H bonds are formed from $sp^{2.1}$ hybrids on carbon. Consistent with this hybridization, the centroid of charge of the bond is located slightly off the C-H axis. The LMOs for the dimer are quite different. Here we see evidence of the electron-deficient nature of these oligomers, as the dominant feature of the bonding is the presence of two three-centered Li-C-Li bonds with the methyl group bridging the two lithium atoms. These three-center bonds are somewhat polar, showing excess density on the carbon. The hybridization at C for this bond is $sp^{3.4}$ while the hybridization on Li is $sp^{1.9}$. The carbon atom hybridization is quite normal and the hybridization on Li shows the large amount of Li(2p) character required for bonding. The location of the centroid of charge (cc) is useful in understanding the type of three-center bond formed. The angle C-Li-cc is small (~3°) while the angle Li-C-cc is larger (~29°). Thus, the Li orbitals are directed toward C along the Li-C axes while the carbon directs its orbital along the bisector of the angle Li-C-Li in order to obtain a maximum overlap with the Li orbitals. This is shown in Figure 3. The three-centered bond formed in this compound is similar to a closed three-center B-B-B bond as opposed to a B-H-B bridge bond or an open B-B-B bond.[4] The C-H bonds in the dimer, with a hybridiation of $sp^{2.1}$ on C and a centroid of charge displaced from the axis, are quite similar to those in the monomer. The bonding in the trimer is comparable to that of the dimer and involves three central Li-C-Li bonds. The major difference is that there is somewhat more Li(2s) character in the Li hybrid orbital, now $sp^{1.5}$. The direction of the hybrid orbital on Li is no longer along the Li-C axis, indicating that the centroid of charge is located further from C than in the dimer. The bonding in the larger planar clusters can be explained, in a similar fashion, by closed three-center Li-C-Li bonds.

The bonding in the condensed structures is clearly different from that found in the planar oligomers. The structural bonding in the T_d tetramer is composed of four four-center bonds each involving three lithiums and one carbon. As shown in Figure 3b, the bonding can be described in terms of closed multicentered bonds. These bonds show a higher amount of C(2s) character and a decrease in Li(2s) character relative to the D_{4h} form. The overall charge distribution between the carbon and the lithiums, however, remains remarkably similar in the T_d and D_{4h} geometries and remains essentially independent of three- or four-center bond formation. We also note a large negative overlap interaction with the lithium not involved in the four-center bond.



3-CENTER BOND 4-CENTER BOND

Figure 3. Schematic representations for multicentered bonds showing three-center and four-center bonds. The three-center bond is typical of the bonding in the planar oligomers while the four-center bond is that found for the tetrahedral T_d isomer.

Although the C_s pentamer structure is not particularly stable, we have also analyzed its bonding in terms of LMOs. The bonding pattern differs from that found for the T_d tetramer, although the location of the methyls in the center of a triangular lithium face is quite similar. Instead of having four-centered bonds as found for the T_d tetramer, most of the bonding in the C_s pentamer is due to closed three-center Li-C-Li bonds with donation from the third lithium in the face. In fact, the unique basal lithium Li(2) does not participate in any of the three-center bonds, but rather serves as an electron-donating center to the four adjacent bonds. This symmetry-unique basal lithium is a fractional center. It donates 0.13 e to each of the two bonds in the lower faces, 3-9-5 and 1-10-5, and also donates 0.20 e to the equivalent 1-7-4 and 3-6-4 bonds in the upper faces. The apex lithium Li(4) donates 0.16 e to the symmetry-unique 3-8-1 bond. The two equivalent methyl groups in the upper face have a more equal distribution of charge between the lithiums directly bonded to them than do the other bonds (see Table X). The two equivalent bonds in the lower faces have more density from the apical than from the basal lithiums.

The pattern of LMOs for the D_{3d} hexamer reveals much about the structure of this molecule. As shown in Figure 2, the bonding takes place about the two open faces. The lithiums around an open face are bound by three bridging methyls utilizing closed three-center Li-C-Li bonds. However, the respective apical Li on the adjacent triangle of lithiums from the other vacant face shows a significant interaction with the central methyl group, donating 0.16 e. In fact, it is the donation bonding from this apical Li that holds the cluster together. We note that the unequal charge distribution between the two lithium triangles for a given three-centered bond arises even though the CH_3 is placed on the center of each occupied triangular face. The $sp^{3.9}$ hybrid on C is similar to that found in the other Li-C-Li bonds previously discussed. These results reinforce the observation suggested by the overlap populations that the D_{3d} hexamer exists as two interacting distorted D_{3h} trimers.

The bonding in the ethyllithium monomer and dimer is similar to that of CH_3Li and $(CH_3Li)_2$, respectively. In C_2H_5Li the methyl substituent about the central ethyl carbon causes the Li–C centroid of charge to be shifted from the Li–C axis while the Li substituent has a similar effect on the C–C bond. For the dimer only a small effect due to the presence of the methyl substituent is seen on the Li–C–Li bonds while the lithiums have little effect on the bonding in the ethyl group.

Conclusions

We have shown that there exist stable oligomers of $(CH_3Li)_n$ for $n = 1$–6 with significant binding energies and that for $n = 4$ and $n = 6$ there are at least two different geometries that yield stable clusters. The calculated ionization potentials and various structural predictions have been used to provide a new interpretation of previous mass-spectral studies. We have investigated the amount of metal–metal bonding through the use of overlap populations and find significant metal–metal interactions in the planar forms, but little intermetallic bonding in the condensed aggregates. The bonding in all of the alkyllithium clusters is interpreted in terms of localized molecular orbitals. The planar forms are bound by a network of closed three-center Li–C–Li bonds. The hybridization on carbon is normal, but the hybridization on Li for $n > 1$ usually has significantly more Li(2p) than Li(2s) character. This shows the large amount of promotion on Li needed for bonding in these clusters. The heavy atoms of the T_d tetramer are connected by closed four-centered bonds, each involving three lithiums and a carbon. The bonding in the D_{3d} hexamer consists of closed three-center Li–C–Li bonds with significant donation from a third lithium. This leads to the conclusion that the hexamer is composed of weakly interacting distorted D_{3h} trimers. Calculations on the monomer and dimer of ethyllithium show that the extra CH_3 substituent on the carbon has very little effect.

Acknowledgments. We thank the Alfred P. Sloan Foundation and Du Pont for support of this research. We also thank the University of Minnesota Computing Center for a grant of computer time.

Supplementary Material Available: Molecular coordinates (5 pages). Ordering information is given on any current masthead page.

Circular Dichroism, Crystal Structure, and Absolute Configuration of the Siderophore Ferric *N*,*N*′,*N*″-Triacetylfusarinine, $FeC_{39}H_{57}N_6O_{15}$

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Received February 4, 1980

Abstract: The siderophore ferric *N*,*N*′,*N*″-triacetylfusarinine ($FeC_{39}H_{57}N_6O_{15}$) was isolated from iron-deficient cultures of an unidentified *Penicillium* species and purified by anion exchange, adsorption, and gel-filtration chromatographies. The chelate was crystallized as the benzene solvate (six to seven molecules of benzene per asymmetric unit) in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell of the dimensions $a = 21.82$ (3), b 23.89 (3), and $c = 14.14$ (1) Å at −135 (2) °C. The intensity data (5669) were collected on a CAD-4 automatic diffractometer, using Mo K$\bar{\alpha}$ radiation at −135 (2) °C. The structure was solved by a Patterson synthesis and successive difference Fourier syntheses, and refined by least-squares methods. The final R values were 0.141 for all data and 0.108 for 4566 observed data. The Fe^{3+} ion is coordinated by the oxygen atoms of the three hydroxamate groups in a distorted octahedron. The molecule is relatively flat with a total thickness of about 4.5 Å; three of the benzene solvent molecules are tucked between the macrocyclic rings. In the crystals obtained from ethanol/benzene, the molecules assume the Λ-cis absolute configuration, as determined from anomalous dispersion and circular dichroism on the solid state; however, in solution, and in the morphologically different crystals from chloroform, the molecule exists predominantly as the Δ-cis diastereoisomer, as determined by circular dichroism.

Introduction

It is well known under iron-limiting conditions (ca. 10^{-7} M Fe) that aerobic microbial growth is facilitated by the elaboration of low molecular weight, Fe(III)-specific sesquestering agents, termed siderophores, responsible for the acquisition and assimilation of iron.[1-3] Seven families of siderophores have been identified, including ferrichromes, ferrioxamines, fusarinines, rhodotorulic acids, aerobactins, enterobactins, and mycobactins. Two types of ligating groups prevail among these families, the hydroxamates and the catecholates, both of which form stable octahedral complexes with iron, where the iron atom is d^5, high spin,[4,5] and readily exchangeable.[6]

The fusarinines are members of a unique class of amino acid esters isolated from various species of fungi.[7-11] The monomeric unit, fusarinine, or N^δ-(*cis*-5-hydroxy-3-methylpent-2-enoyl)-N^δ-hydroxy-L-ornithine, has been isolated from *Fusarium roseum*.[7] Fusarinine undergoes polymerization via the formation of head-to-tail ester linkages (aminoacyl bonds) rather than the peptide bonds more common to other siderophores. Fusarinine C[7] or fusigen,[9] the cyclic triester of fusarinine, is thought to be the ferric ionophore for *F. roseum*. However, owing to the extreme lability of the aminoacyl bonds of fusarinine C, efforts to characterize this siderophore have been limited.

The *N*-acetyl analogue of fusarinine, or N^α-acetyl-N^δ-(*cis*-5-hydroxy-3-methylpent-2-enoyl) N^δ-hydroxy-L-ornithine, has been

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0002-7863/80/1502-5766$01.00/0