Organometallics 1988, *7*, 1597-1607

Methyllithium and Its Oligomers. Structural and Energetic Relationships

Elmar Kaufmann,[†] Krishnan Raghavachari,[‡] Alan E. Reed,[†] and Paul von Ragué Schleyer[*†]

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany, and AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Received December 30, 1987

Reliable structural and energetic data for methyllithium oligomers $(CH_3Li)_n$, $n = 1–4$, have been obtained by ab initio calculations using relatively large basis sets and including correlation and zero point energy corrections. The association energies for the dimer, trimer, and tetramer are −44.3, −79.0, and −122.9 kcal/mol, respectively. Monomeric methyllithium in the gas phase is indicated to be 88% ionic by natural population analysis and can well be described as a lithium cation stabilized methyl anion. The estimated heat of formation, $\Delta H_f{}^\circ{}_0 = 26.9 \pm 0.5$ kcal/mol, corresponds to a bond dissociation energy, $D_0(H_3C–Li) = 46.4 \pm 2.5$ kcal/mol. The bonding in methyllithium oligomers is largely electrostatic. Li–H ("agostic") interactions are responsible for the eclipsed conformation of tetrameric methyllithium in the gas phase. The staggered conformation found experimentally in the solid state is due to a packing effect involving interaggregate interactions. Rotation barriers of alkyl groups in $(RLi)_4$ are about 1 ($R = CH_3$) and 2 ($R = C_2H_5$) kcal/mol. Equilibria between dimers, trimers, and tetramers have been modeled by the semiempirical MNDO method using statistical thermodynamics and including solvation effects. Whereas trimers are favored over dimers in the gas phase, the opposite is true in solution. If tetramers dissociate to smaller aggregates in donor solvents, only dimers are expected. The experimentally known negative temperature dependence of the equilibrium $(RLi)_4 \rightleftharpoons 2(RLi)_2$ in solution is confirmed to be due to entropy. The inversion of alkyl groups in alkyllithium clusters does not involve dissociation or free carbanions but proceeds via polycoordinate carbon species with the critical substituents in a plane. The activation energy for this process in the tetramer is estimated to be 14.3 kcal/mol.

Introduction

Methyllithium, the simplest organolithium compound, was first prepared by Schlenk and Holtz in 1917.[1] Like the other alkyllithiums which were reported in the same paper, CH_3Li has now gained considerable importance in organic and organometallic synthesis.[2,3] It is frequently used for methylations, e.g. for additions to carbonyl groups and to α,β-unsaturated aldehydes and ketones, and for halogen replacement in transition-metal chemistry. The first homoleptic transition-metal complexes were prepared by this method.[4] The methyl cuprates,[5] which result from the reaction of copper halides and methyllithium, also are valuable reagents because of their greater selectivity.

Investigations of the structure of methyllithium began long after the synthetic potential of alkyllithiums had been explored. The assignments of IR spectra made between 1957 and 1963[6] were not definitive but did indicate that CH_3Li does not exist as a monomer even in the gas phase.[6c] In 1964, Weiss and Lucken[7a] deduced the structure of methyllithium from its X-ray powder diffraction pattern; this was refined in 1970.[7b] CH_3Li consists of tetrameric units of the type found first by Dietrich in 1963 in the single-crystal X-ray structure of ethyllithium.[8] The methyl groups in $(CH_3Li)_4$ bridge the faces of a lithium tetrahedron, and the hydrogens are staggered with respect to the corresponding Li_3 site.[7] The tetramers persist in solution, even with strong donors. This has been shown by colligative property measurements[9] and by means of ^1H, ^7Li, and ^{13}C NMR.[10,11] Tetramers are present even in the gas phase, as has been shown recently by Lagow's group[12a] using a flash vaporization technique. Similar results have been obtained by Plavšić et al.[12b] In 1966, however, T. L. Brown presented evidence for an equilibrium between tetramers and dimers in ether solution.[10] The observed fractional orders for organolithiums in the kinetic equations of metalation and addition reactions led to the suggestion (erroneous, as later found) that monomers might be the reactive species.[13]

Andrews measured the IR spectrum of monomeric methyllithium in an argon matrix in 1967.[14] Some of the earlier assignments[6] had to be revised. Especially noteworthy was the low H–C–Li bending force constant and high dipole moment (6 D) which indicated the large ionic character of the C–Li bond.[14]

X-ray crystal structures of methyllithium derivatives include mixed tetramers with ethyllithium[15] and tetrameric

---

[†] Universität Erlangen-Nürnberg.

[‡] AT&T Bell Laboratories.

(1) Schlenk, W.; Holtz, J. *Ber. Dtsch. Chem. Ges.* **1917**, *50*, 262.

(2) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974.

(3) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley-Interscience: New York, 1979.

(4) Shortland, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1972**, 318. Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209. Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39.

(5) House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911; **1968**, *90*, 5615. Also see ref 27.

(6) (a) Brown, T. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1957**, *79*, 1859. (b) Shigorin, D. N. *Spectrochim. Acta* **1959**, *14*, 198. (c) West, R.; Glaze, W. *J. Am. Chem. Soc.* **1961**, *83*, 3580. (d) Goubeau, J.; Walter, K. *Z. Anorg. Allg. Chem.* **1963**, *322*, 58.

(7) (a) Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* **1964**, *2*, 197. (b) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265.

(8) Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681. Dietrich, H. *J. Organomet. Chem.* **1981**, *205*, 291.

(9) West, P.; Waack, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395.

(10) Seitz, L. M.; Brown. T. L. *J. Am. Chem. Soc.* **1966**, *88*, 2174. Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4134. Also see: Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4140.

(11) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057.

(12) (a) Landro, F. J.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Organomet. Chem.* **1983**, *249*, 1. Chinn, J. W., Jr.; Lagow, R. J. *Organometallics* **1984**, *3*, 75. (b) Plavšić, D.; Srzić, D.; Klasinc, L. *J. Phys. Chem.* **1986**, *90*, 2075.

(13) West, P.; Waack, R.; Purmort, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840 and references therein. Waack, R.; Stevenson, P. E. *J. Am. Chem. Soc.* **1965**, *87*, 1183.

(14) Andrews, L. *J. Chem. Phys.* **1967**, *47*, 4834.

(15) Weiss, E. *Chem. Ber.* **1964**, *97*, 3241.

0276-7333/88/2307-1597$01.50/0 © 1988 American Chemical Society

Table I. MNDO Heats of Formation (kcal/mol) and Total Energies (au) of Methyllithium Oligomers at Various Levels

species		point group	MNDO	STO-3G// STO-3G	3-21G// 3-21G	6-31G[a]	MP2/ 6-31G[a]	6-31G+6d(C)[b]	MP2/ 6-31G*[b]
CH_3Li	**1a**	C_{3v}	-1.4	-46.421 59[c]	-46.752 48[c]	-47.003 30	-47.106 09	-47.015 54[c,d]	-47.162 00
	1b	C_{2v} planar	+42.3	-46.338 05[c,e]	-46.693 07[c,e]			-46.959 26[c-e]	-47.112 70
$(CH_3Li)_2$	**2a**	C_{2h} eclipsed	-75.0	-92.906 86[f]	-93.578 68	-94.073 12	-94.277 52	-94.098 93[d]	-94.396 42
	2b	C_{2h} staggered	-75.0		-93.578 65				
	2c	C_{3v} linear	-28.4		-93.540 42			-94.062 79[d]	-94.360 50
	2d	C_s one methyl planar	-36.3[e]	-92.883 80[f]	-93.545 58[e]	-94.039 02	-94.249 37	-94.065 17[d]	-94.369 87
$(CH_3Li)_3$	**3a**	C_{3h}	-132.1	-139.399 42	-140.400 70	-141.138 76	-141.449 54	-141.174 47	
	3b	C_{3v} linear			-140.335 40	-141.078 08	-141.388 84	-141.114 06	
	3c	C_{2v} one methyl planar	-105.1[e]	-139.392 20	-140.378 56	-141.116 72	-141.430 39	-141.150 44	
$(CH_3Li)_4$	**4a**	T_d eclipsed	-213.2	-185.887 39[g]	-187.229 88	-188.208 23	-188.628 85	-188.257 24	
	4b	T_d staggered	-205.4	-185.858 30[g]	-187.225 30	-188.203 25	-188.620 15	-188.250 13	
	4c	C_{4h}	-177.7[e]	-185.880 17	-187.209 41	-188.192 57	-188.610 21	-188.240 50	
	4d	C_{2v} two methyls planar	-136.1	-185.892 10	-187.186 32	-188.171 74	-188.590 02	-188.214 11	

[a] Species **1** and **2** in 6-31G and **3** and **4** in 3-21G geometry. [b] Species **1** and **2** in 6-31G* and **3** and **4** in 3-21G geometry. [c] Taken from ref 47. [d] Full 6-31G* basis set. [e] Transition structure (characterized by one negative eigenvalue of the force constant matrix). [f] Taken from ref 24. [g] Reoptimized from ref 24.

methylsodium containing variable amounts of $(CH_3Li)_4$ units.[16] In a CH_3Li crystal structure containing tetramethylethylenediamine (TMEDA), the tetrameric units are not disrupted despite the presence of a strongly chelating agent.[17] Recently, monomeric[18] and dimeric[19] alkyllithium derivatives have been characterized; these contain bulky substituents or carbanion stabilizing groups or involve donor solvents or chelating agents. Other studies on methyllithium include the ESR spectrum of the radical obtained by hydrogen abstraction from the tetrameric unit[20] and a valence X-ray photoelectron spectrum.[21]

Earlier Calculations on $(CH_3Li)_n$

Methyllithium and its oligomers have also been the subject of numerous theoretical studies concerning their structures, energies, and bonding.[22-35] However, these often disagree in detail and none are both comprehensive and definitive.

Early calculations[22] either were of semiempirical type or did not involve full geometry optimizations but showed clearly the strong tendency of CH_3Li to oligomerize. Several papers[23-25] presented minimal basis ab initio calculations on the dimer and tetramer. The question of methyl orientation in the tetrahedral tetramer with respect to the Li_3 site also was addressed, but, in contrast to the experimental result, the eclipsed conformation was found to be more favorable.[23,24] Planar eight-membered rings as alternative structures for the tetramer have been considered.[26-28] Whereas the semiempirical methods[26,27] actually favored the planar structure, the ab initio calculations[27,28] predicted the tetrahedral cluster to be more stable, in accordance with the X-ray studies.[7] The energy differences, however, appear to be rather small. The possibility that the stereomutation of prochiral $LiCH_2$ groups, as observed by NMR,[36,37] might take place in planar ring aggregates, has been proposed.[24,33a]

The extent of ionicity of the carbon–lithium bond has been a question of central interest and continuing debate.[19a,29-32] X-ray electron density difference maps were not able to distinguish between an ionic or covalent nature of this bond.[19a] Streitwieser et al.[29] claimed essentially ionic bonding in methyllithium monomer (charge on Li +0.8 electron) based on electron density projection functions[29a] and rationalized the tetrameric structure of solid CH_3Li by a totally ionic model.[29b] The "best fit radii" of Hehre et al.[30] indicate the bonding in CH_3Li to be largely ionic, but not to the extent as in LiF, LiOH, and $LiNH_2$. Using different criteria (dipole moments and comparison with ionic and covalent models), Lipscomb et al.[31] suggested a charge separation of about 0.6 electron in CH_3Li. Schiffer and Ahlrichs[32] concluded "covalent contributions to the C–Li bond in MeLi to be more pronounced and more important than even for LiCl". At present there seems to be agreement that *all* organolithium compounds

---

(16) Weiss, E.; Sauermann, G.; Thirase, G. *Chem. Ber.* **1983**, *116*, 74.

(17) Köster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1.

(18) (a) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323. (b) In tetrahydrofuran, *tert*-butyllithium is a monomer and 2-butyllithium a dimer–monomer mixture: Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.

(19) (a) Amstutz, R.; Laube, T.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1984**, *67*, 224. (b) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117. For a review of organolithium compounds see: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(20) Chen, K. S.; Bertini, F.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1340.

(21) Meyers, G. F.; Hall, M. B.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1413.

(22) (a) Cowley, A. H.; White, W. D. *J. Am. Chem. Soc.* **1969**, *91*, 34. (b) Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Organomet. Chem.* **1972**, *44*, 59. (c) Baird, N. C.; Barr, R. F.; Datta, R. K. *J. Organomet. Chem.* **1973**, *59*, 65.

(23) McLean, W.; Pedersen, L. G.; Jarnagin, R. C. *J. Chem. Phys.* **1976**, *65*, 2491.

(24) Clark, T.; Schleyer, P. v. R.; Pople, J. A. *J. Chem. Soc., Chem. Commun.* **1978**, 137. Also see: Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1980**, 672.

(25) McLean, W.; Schultz, J. A.; Pedersen, L. G.; Jarnagin, R. C. *J. Organomet. Chem.* **1979**, *175*, 1.

(26) Graham, G.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 5759.

(27) Stewart, K. R.; Lever, J. R.; Whangbo, M.-H. *J. Org. Chem.* **1982**, *47*, 1472.

(28) Herzig, L.; Howell, J. M.; Sapse, A. M.; Singman, E.; Snyder, G. *J. Chem. Phys.* **1982**, *77*, 429.

(29) (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *156*, 1.

(30) Francl, M. M.; Hout, R. F., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 563. Also see ref 34.

(31) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 4572.

(32) Schiffer, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1986**, *124*, 172.

(33) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151. (b) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909. (c) Bader, R. F. W.; MacDougall, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 6788.

(34) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(35) (a) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856. (b) Hodošček, M.; Šolmajer, T. *J. Am. Chem. Soc.* **1984**, *106*, 1854.

(36) Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 737.

(37) Fraenkel, G.; Beckenbaugh, W. E.; Yang, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 6878. Fraenkel, G.; Dix, D. T.; Carlson, M. *Tetrahedron Lett.* **1968**, 579.

Table II. Relative Energies (kcal/mol) of Methyllithium Oligomers at Various Levels[a]

species		point group	MNDO	STO-3G// STO-3G	3-21G// 3-21G	6-31G	MP2/ 6-31G	6-31G+6d(C)	MP2/ 6-31G*	final est[b]
CH_3Li	**1a**	C_{3v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1b	C_{2v} planar	43.7	52.4	37.3			35.3	30.9	30.9
$(CH_3Li)_2$	**2a**	C_{2h} eclipsed	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	2b	C_{2h} staggered	0.0		0.02					
	2c	C_{3v} linear	46.6		24.0			22.7	22.5	22.5
	2d	C_s one methyl planar	38.7	14.5	20.8	21.4	17.7	21.2	16.7	16.7
$(CH_3Li)_3$	**3a**	C_{3h}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	3b	C_{3v} linear			41.0	38.1	38.1	37.9		37.9
	3c	C_{2v} one methyl planar	27.0	4.5	13.9	13.8	12.0	15.1		13.3
$(CH_3Li)_4$	**4a**	T_d eclipsed	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	4b	T_d staggered	7.8	18.3	2.9	3.1	5.5	4.5		6.9
	4c	C_{4h}	35.5	4.5	12.8	9.8	11.7	10.5		12.4
	4d	C_{2v} two methyls planar	77.1	−3.0	27.3	22.9	24.4	27.1		28.6

[a] Calculated by using the energies from Table I. [b] Final estimate evaluated adding the MP2 corrections to the HF results, each at the highest levels employed.

Table III. Structures, Charges, and Dipole Moments for Methyllithium at Various Levels[a,b]

	geometries			charges[c]		charges[d]	charges[e]		
	C–Li	C–H	Li–CH	Li	C	Li	Li	C	dipole moments
MNDO	1.821	1.117	112.0	+0.421	−0.307				5.63
HF/STO-3G	2.009	1.083	112.6	+0.158	−0.242		+0.465	−0.505	4.27
HF/3-21G	2.001	1.094	111.9	+0.520	−0.905	+0.794[f]	+0.811	−1.362	5.50
HF/6-31G	1.996	1.093	111.4	+0.485	−0.799		+0.821	−1.425	5.61
HF/6-31G*	2.001	1.093	112.6	+0.574	−0.781	+0.797	+0.822	−1.392	5.72
HF/6-31+G*	2.002	1.094	112.5	+0.373	−0.825		+0.865	−1.448	5.98
HF/6-31++G**	2.003	1.094	112.2	+0.401	−0.561				6.01
HF/6-311G*[g]				+0.535	−1.057		+0.869	−1.336	5.90
HF/6-311+G**[g]				+0.521	−0.750		+0.882	−1.369	6.00
MP2/6-31G*	2.003	1.099	112.0						
MP2/6-311G*	1.983	1.098	112.6						

[a] Presented in part in ref 34. For other values calculated at various levels, see ref 29a and 32. [b] Bond lengths in Å, angles in deg, and dipole moments in D. [c] Mulliken population analysis. [d] Integrated spatial electron populations.[52] [e] Natural population analysis.[53a] [f] 4-31G data. [g] MP2/6-311G* geometry.

are predominately ionic with small but nonnegligible covalent contributions.[31-34] The dimerization energies of lithium compounds are governed by the electronegativities of the groups attached to lithium.[35a] Energy decomposition analyses show the electrostatic contribution to be the dominant term.[35b]

This work is an extension of our studies of aggregation of lithium compounds.[34,35a,38] We present higher level ab initio calculations of methyllithium oligomers up to the tetramer and provide reliable structural and energetic data. The questions of inversion and rotation of the methyl groups within the clusters are also addressed. The equilibria between clusters of different size including solvent effects are examined by means of semiempirical calculations.

Calculational Methods

Calculations were carried out at the restricted Hartree–Fock (HF)[39] level by using various versions of the GAUSSIAN series of programs[34,40] and, in most cases, standard basis sets (e.g. minimal STO-3G,[41] split valence 3-21G,[42] 6-31G,[43] polarization 6-31G*,[43] etc.[34]). The structures were completely optimized within the indicated symmetry constraints by using gradient optimization techniques.[44] Electron correlation effects were calculated with the 6-31G* or 6-31G basis set by using Møller–Plesset theory[45] carried out to second order (MP2). Higher level single points on the trimers and tetramers were done at the HF/6-31G level by using six additional d functions on carbon (but not on lithium). This basis set is designated 6-31G+6d(C). The omission of polarization functions on lithium does not change the *absolute* energies very much (0.3 and 2.3 kcal/mol at the HF and MP2 levels, respectively, in the case of CH_3Li), and the *relative* energies should be influenced very little.[46] Some of the total energies listed in Table I were taken from the Carnegie-Mellon Quantum Chemistry Archive.[47] Semiempirical

---

(38) Sapse, A.-M.; Kaufmann, E.; Schleyer, P. v. R.; Gleiter, R. *Inorg. Chem.* **1984**, *23*, 1569. Sapse, A.-M.; Raghavachari, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Am. Chem. Soc.* **1985**, *107*, 6483. Also see: Raghavachari, K.; Sapse, A.-M.; Jain, D. C. *Inorg. Chem.* **1987**, *26*, 2585.

(39) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(40) GAUSSIAN 76: Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *14*, 368. GAUSSIAN 82: Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R., Carnegie-Mellon University. See ref 34. We thank A. Sawaryn and T. Kovář for their contributions to the version of the program used in Erlangen. The latest calculations were carried out on a Convex C1 computer using the GAUSSIAN 82 version provided by the Convex Computer Corp.

(41) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769.

(42) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(43) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *26*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(44) Davidon–Fletcher–Powell algorithm: Davidon, W. C. *Comput. J.* **1968**, *10*, 406. Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. Poppinger, D. *Chem. Phys. Lett.* **1975**, *34*, 332. Schlegel's algorithm: Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(45) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229 and references therein.

(46) Kaufmann, E.; Schleyer, P. v. R., manuscript in preparation.

(47) *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA.

calculations were done with the MNDO[48] approximation using the MOPAC and AMPAC programs.[49] The MNDO heats of formation (298 K, gas phase) are included in Table I. Zero point energies (ZPE) were calculated at the 3-21G (monomer, dimer) or MNDO (trimer, tetramer) level and scaled by the empirical factor 0.9.[34,50] MNDO zero point energies are comparable with ab initio values.[51] Final estimates of relative energies (Table II) and of reaction energies were obtained by adding the MP2 corrections to the HF results, each at the highest levels employed. Association reactions also were corrected for differences in ZPEs. Full geometry information in the form of archive entries[47] or "Z matrices" for all the species calculated ab initio is available as supplementary material.

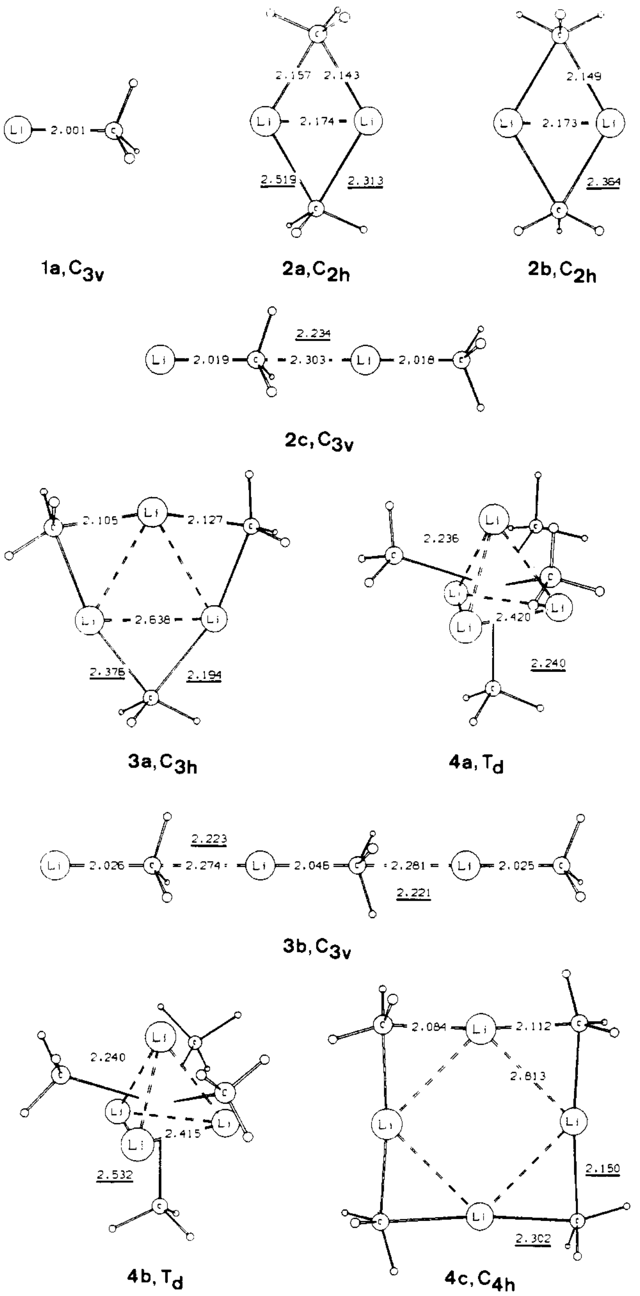


Figure 1. Structures of methyllithium oligomers (3-21G basis, distances in Å). Underlined numbers correspond to Li–H separations.

Monomeric Methyllithium

At most ab initio levels examined, C_{3v} CH_3Li **1a** (Figure 1) has a C–Li bond length of 2.000 ± 0.004 Å; C–H is 1.096 ± 0.003 Å and the H–C–Li angle 112.0 ± 0.7°. These averages come from calculations with and without correlation using different basis sets, but the 1.983-Å C–Li distance at MP2/6-311G* is somewhat shorter. Table III shows that there is only a small dependence of geometry on the theoretical level; even the small split valence basis set 3-21G gives good results. This is generally the case in organolithium systems, provided there are no heteroatoms. Our C–Li values are slightly larger than those derived by Schiffer and Ahlrichs[32] using large basis sets at the SCF (1.993 Å) and correlated (1.977 Å) levels. The calculated dipole moments in the range of 5.50–6.01 D (the minimal basis STO-3G value is too low) are somewhat more basis set dependent than the geometry but are in reasonable agreement with that deduced by Andrews (6 D)[14] in his matrix-isolation study or calculated by Lipscomb (5.4 D)[31] with a near Hartree–Fock limit basis set and large CI (on an assumed geometry with C–Li = 2.021 Å, however). The most elaborate calculation of methyllithium carried out to date by Schiffer and Ahlrichs[32] yields 5.70 D. The atomic charges obtained by Mulliken population analysis are very basis set dependent (Li +0.37 to +0.57, C −0.56 to −1.06), a well-known deficiency of this method. Streitwieser's "integrated spatial electron populations" method[52] and the recently introduced "Natural population analysis" (NPA)[53a] which overcomes most of the basis set dependence both yield a charge of +0.8 for lithium with moderately large basis sets. Since the CH_3 group in CH_3Li is found to carry nearly a full negative charge, the carbon lone-pair orbital is rather diffuse. Consequently, a significant increase in the NPA (or "natural") charge on lithium occurs, to +0.865, when diffuse (+) functions are added to carbon and lithium (6-31+G* basis). In basis sets without diffuse functions, the lithium functions thus help to describe the carbon lone-pair orbital (basis set superposition error, BSSE).[54] However, Table III indicates that the geometry of CH_3Li is hardly affected by the diffuse functions. Further extension of the basis set leads to only slightly more ionic values of the natural charge at lithium, e.g., +0.882 using the 6-311+G** basis set. The ionic character of CH_3Li thus approaches a limit of 88% by the NPA method, compared to 98% for LiF (at the 6-31+G* level). Thus, methyllithium is a highly polar species, which is expected to oligomerize readily due to the strong electrostatic attractions.

---

(48) MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. Li parametrization: Thiel, W.; Clark, T., unpublished results.

(49) MOPAC: Stewart, J. J. P. *QCPE* **1985**, *5*, 455. AMPAC: Stewart, J. J. P. *QCPE Bull.* **1986**, *6*, 506.

(50) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225. Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269. DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333. Also see: Komornicki, A.; Pauzat, F.; Ellinger, Y. *J. Phys. Chem.* **1983**, *87*, 3847.

(51) The MNDO and 3-21G values are 22.0 and 22.4 kcal/mol for the monomer and 45.6 and 46.0 kcal/mol for the dimer, respectively. The trimer and tetramer have zero point energies of 69.1 and 94.1 kcal/mol, respectively, at the MNDO level.

(52) Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81.

(53) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1986**, *84*, 2428. (e) The NPA/NBO/NLMO analyses presented in this work were performed with a slightly modified version (to allow the dipole moment analysis) of Quantum Chemistry Program Exchange program 504: Reed, A. E.; Weinhold, F. *QCPE Bull.* **1985**, *5*, 141.

(54) Kolos, W. *Theor. Chim. Acta* **1979**, *51*, 219 and references therein. Also see: Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283.

Through the natural population,[53a] the natural hybrid (NHO) and bond orbital (NBO),[53b] and the natural localized molecular orbital (NLMO)[53c] analysis methods, one can perform an additive decomposition of the molecular dipole moment of SCF wave functions.[53d] Through the recent application of this method to methane, the inaccuracy of directly relating bond dipole moments to bond polarity has been demonstrated.[53d] Such an NPA/NHO/NBO/NLMO analysis of the dipole moment (and also of higher moments, particularly the quadrupole) yields a more refined picture of the electron distribution than is possible through an atomic population analysis. We have therefore analyzed the dipole moment of the 3-21G//3-21G wave function for CH_3Li.[53e]

The total dipole moment μ_{tot} was found to be 5.51 D, 1.45 D of this being from the component of the three σ_{CH} NLMO bond dipoles along the molecular symmetry axis and the other 4.06 D from the σ_{CLi} NLMO. As in CH_4, the C–H bond dipoles in CH_3Li are oriented C^+H^-, hence these C–H bond dipoles *enhance* μ_{tot}. The σ_{CLi} NLMO dipole moment may be decomposed conveniently into four terms: (1) an ionic dipole with a single negative charge at C and a positive charge at Li, giving $\mu(1)_{CLi}$ = +9.61 D, (2) the dipole moment of the carbon lone-pair natural hybrid orbital (NHO) with respect to the carbon nucleus, multiplied by the NHO occupancy of 1.817, giving $\mu(2)_{CLi}$ = −3.26 D, (3) the dipole moment of the lithium valence NHO with respect to the carbon atom, multiplied by the NHO occupancy of 0.183, giving $\mu(3)_{CLi}$ = −1.73 D, and (4) the contribution to the dipole moment from the "interference" of the carbon lone-pair NHO and the lithium valence NHO (this arises from the off-diagonal element of the dipole moment operator between these two NHOs; for details, see ref 53d), giving $\mu(4)_{CLi}$ = −0.55 D. The simplest approach to the C–Li bond dipole would only consider the fully ionic term (1) and the covalent correction term (3), calculating the bond dipole based on the natural atomic charge on Li of +0.81 (3-21G). This approach would be rather inaccurate because the anionic carbon lone pair is diffuse and directed toward the Li atom, as is shown by term (2). Indeed, the centroid of the carbon lone pair NHO is 0.37 Å from the carbon nucleus oriented toward lithium! The interference dipole term (4) also acts to decrease the net C–Li bond moment. The reason for this is that, when one atom of a bond employs an sp hybrid (such as C) and the other atom an unhybridized nodeless s orbital (H or Li), the interference dipole term tends to direct the bond orbital centroid toward the latter atom.[53d] Thus, the C–Li bond moment can be overestimated by roughly a *factor of 2* when one considers only the atomic charges from the population analysis, i.e., terms (1) and (3). The basis set dependence of this dipole moment analysis was probed by employing the HF/6-31+G*//HF/6-31G* wave function for CH_3Li: essentially similar results are obtained with μ_{tot} = 5.98 D, μ_{CLi}(NLMO) = 4.33 D, and $\mu(1)_{CLi}$ through $\mu(4)_{CLi}$ = +9.61, −3.39, −1.30, and −0.60 D, respectively.

Thus, methyllithium is well-represented as a lithium cation-stabilized methyl anion. While the stabilization is primarily electrostatic, a small but important charge transfer or covalent component is present as well. This gegenion stabilization is evident when one compares the energy of the HOMO of CH_3Li with that of the methyl anion (−0.27 vs +0.05 au, 3-21G level). Indeed, MCSCF calculations indicate that the methyl anion is barely bound and probably occupies a diffuse Rydberg orbital.[55] The stabilization of the lone-pair orbital of CH_3^- by Li^+ is obviously much less than that by H^+ (to form CH_4); the energy of the HOMO of CH_4 is much lower, being −0.54 au at 3-21G.

Table IV. Calculated and Experimental Vibrational Frequencies (cm^{-1}) of Monomeric Methyllithium

mode		calcd[a]	calcd[b]	exptl[c]
$\nu_1(a_1)$	C–H symm stretch	3102	3021	2780
$\nu_2(a_1)$	CH_3 umbrella mode	1237	1164	1158
$\nu_3(a_1)$	C–Li stretch	640	628	530
ν_4(e)	C–H asymm stretch	3152	3106	2820
ν_5(e)	H–C–H bending	1594	1510	1387
ν_6(e)	H–C–Li bending	487	462	409

[a] At HF/6-31+G*.[56] [b] At MP2/6-311G*. [c] Reference 14.

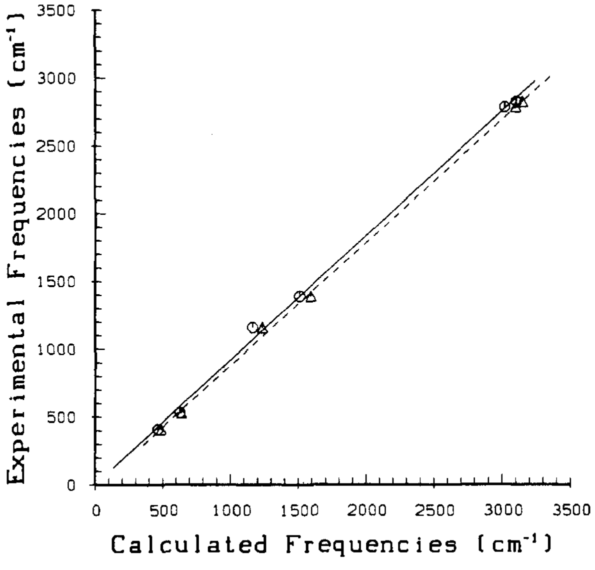


Figure 2. Comparison of calculated (at HF/6-31+G* and MP2/6-311G*) and experimental[14] vibrational frequencies of monomeric methyllithium. The correlation lines have slopes of 0.904 (triangles and dashed line) and 0.916 (circles and solid line), respectively.

The calculated vibrational frequencies of CH_3Li (at HF/6-31+G*)[56] agree very well with those measured by Andrews[14] (Table IV). The correlation line (Figure 2, triangles and dashed line) has a slope of 0.904, a value already recommended for scaling of calculated harmonic frequencies,[34,50] which are generally too high. At MP2/6-311G* this scaling factor is higher, 0.916 (Figure 2, circles and solid line). This again shows that frequencies obtained at the Hartree–Fock level generally are adequate.[34] All of Andrews' assignments made in 1967[14] can now be confirmed definitively, especially his conclusion that the doubly degenerate asymmetric C–H stretching mode is higher in energy than the symmetric one. As mentioned above, his estimate of 6 D for the CH_3Li dipole moment also agrees with the theoretical values (see Table III).

Heat of Formation of Monomeric Methyllithium in the Gas Phase. Since thermochemical measurements on organolithium compounds are rather difficult, very few such data are available.[10,57,58] Calculations provide an alternative approach to this problem.[34] The heat of formation of a given species can be obtained by calculating

---

(55) Kalcher, J.; Janoschek, R. *Chem. Phys.* **1986**, *104*, 251.

(56) Quantum Chemistry Archive of the Friedrich-Alexander-Universität Erlangen-Nürnberg, unpublished results. 6-31+G* frequencies of CH_3Li: Kovář, T., personal communication.

(57) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970. Brubaker, G. R.; Beak, P. *J. Organomet. Chem.* **1977**, *136*, 147 and references therein.

(58) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 3345.

Table V. Reaction Energies (kcal/mol) for Hydrogenolysis and C–Li Dissociation of Methyllithium at Various Levels[a]

equation basis set	HF	MP2	MP3	MP4SDTQ	Δ(ZPE)[b,d]	final est[c,d]
$CH_3Li + H_2 \rightarrow CH_4 + LiH$ (1)						
6-31+G*	−20.24	−12.12	−13.34	−12.30		
6-311+G**	−18.93	−10.82	−12.65	−12.17	+2.96 ± 0.24	−9.21 ± 0.54
$CH_3Li \rightarrow CH_3^\bullet + Li^\bullet$ (2)						
6-311+G**	+16.65	+43.97	+42.37	+44.18	−2.10 ± 0.62	+42.08 ± 1.91

[a] Reference energies taken from ref 47. [b] Difference in zero point energies; average of calculated (scaled by 0.9[50]) and experimental[14,59] values. [c] Final estimate evaluated adding Δ(ZPE) to the MP4SDTQ results. [d] For details (error bars etc.) see the text.

the enthalpy of a reaction involving this species where the heats of formation of all other molecules are known experimentally. The hydrogenolysis of methyllithium (eq 1) is suited for this purpose.[34] The reaction energies,

$$CH_3Li + H_2 \rightarrow CH_4 + LiH \qquad (1)$$

calculated at various levels,[47,56] are shown in Table V. Correlation is very important (energy changes of 7–8 kcal/mol), whereas the HF data with the polarized triple split valence 6-31+G* and the quadruple split valence 6-311+G** basis sets agree within 1.3 kcal/mol. At the MP4SDTQ level, the data converge with a small estimated error (MP3-MP4 difference at 6-311+G**): $\Delta E = -12.17 \pm 0.48$ kcal/mol. Considering the difference in zero point energies, Δ(ZPE) = +2.96 ± 0.24 kcal/mol (average of calculated and experimental[14,59] vibrational frequencies), one gets the heat of reaction at 0 K, $\Delta H_{r0} = -9.21 \pm 0.54$ kcal/mol. Equation 1 and the experimental heats of formation, $\Delta H_f{}^\circ{}_0$, of H_2, CH_4, and LiH (0.00, −15.99 ± 0.08 and +33.65 ± 0.01 kcal/mol, respectively)[59] yield for gaseous monomeric methyllithium $\Delta H_f{}^\circ{}_0(CH_3Li) = +26.87 \pm 0.55$ kcal/mol. MNDO, whose lithium parametrization[48] is a compromise, overestimates the strength of the carbon–lithium bond by about 28 kcal/mol; the MNDO heat of formation of methyllithium, −1.4 kcal/mol (Table I), is much too low. This deficiency should be kept in mind when MNDO is used for structural investigations in organolithium chemistry.

With the experimental heats of formation of the methyl radical and lithium atom, $\Delta H_f{}^\circ{}_0 = 35.62 \pm 0.19$ and 37.69 ± 2.39 kcal/mol,[59] respectively, a C–Li bond dissociation energy in methyllithium (eq 2), $D_0(H_3C{-}Li) = 46.44 \pm 2.46$ kcal/mol, is obtained. A direct calculation (evaluated in

$$CH_3Li \rightarrow CH_3^\bullet + Li^\bullet \qquad (2)$$

analogy to above) yields 42.08 ± 1.91 kcal/mol (see Table V). This value is close to that obtained recently by Schiffer and Ahlrichs (43.7 ± 1.2 kcal/mol).[32] We assume our indirectly derived value to be more accurate, since the evaluation of reaction energies involving closed- and open-shell species (eq 2) is very difficult and needs extremely sophisticated levels of theory. Bond dissociation energies, e.g., are generally underestimated.[34] Our previous estimates for the heat of formation and the C–Li bond dissociation energy of CH_3Li were 28 and 45 kcal/mol, respectively.[60]

Oligomerization Energies

The structures of the methyllithium oligomers considered are shown in Figure 1; their relative energies are given in Table II. The most stable dimer has a C_{2h} geometry **2a** with the planar Li_2C_2 ring eclipsed to the methyl groups. The corresponding staggered C_{2h} dimer **2b** has nearly the same energy (0.02 kcal/mol higher at 3-21G//3-21G). Thus, rotation of the methyl groups is nearly free. The C_{3h} geometry for the trimer **3a** is analogous to that of the best dimer **2a**. Dimers or trimers with linear heavy-atom backbones, **2c** and **3b**, respectively, are not competitive but still have surprisingly high oligomerization energies (−21.8 and −41.1 kcal/mol, which are roughly half that for **2a** and **3a**, respectively). Isomers **2c** and **3b** are stabilized by Li–H interactions, which have also been discussed in relation to X-ray results.[61] The central methyl groups in **2c** and **3b** remain pyramidal, in contrast to the planar arrangement favored in $LiCH_3Li^+$.[62]

Several structures for the tetramer have been considered: the tetrahedral clusters **4a** and **4b** with eclipsed and staggered methyl groups, respectively, and the eight-membered ring species **4c** (C_{4h} point group). The star shape of **4c** with bent-in lithium atoms is noteworthy. A linear tetramer is not expected to exhibit new bonding features compared to the analogous dimer and trimer structures and therefore was not investigated. Although it should be a rather uncompetitive $(CH_3Li)_4$ isomer with a length of about 15 Å and a dipole moment of about 30 D, a recent X-ray structure of benzyllithium shows such linear polymer chains.[19b]

The relative energies of **4a**, **4b**, and **4c** at the highest level employed are 0.0, 6.9, and 12.4 kcal/mol, respectively. Thus, the most stable structure **4a** does *not* have the staggered methyl orientations found in the crystal. The reason for this discrepancy seems to be steric. In the solid, the lithium atoms of a tetrameric unit are "coordinated" by TMEDA[17] or by the methyl groups of neighboring clusters,[7] in just the manner shown by structure **2c** (picture each CH_3Li to be part of a tetramer unit). Modeling this situation by MNDO calculations on a free tetramer and a tetramer solvated with, e.g. ammonia at each of the lithiums, shows a reversal of the relative energies, and the staggered conformation becomes more stable than the eclipsed (see below).

The relative energy of the planar isomer **4c** is remarkably low (12.4 kcal/mol). This might be a model transition structure for the frequently observed intraaggregate exchange of lithium and alkyl groups in alkyllithium oligomers.[37,58] Indeed, at the MNDO level it is a true transition structure (one imaginary frequency) corresponding to this process. Tetramers of this type have been observed for lithium amide derivatives,[63] organocopper and orga-

---

(59) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

(60) Würthwein, E.-U.; Sen, K. D.; Pople, J. A.; Schleyer, P. v. R. *Inorg. Chem.* **1983**, *22*, 496.

(61) Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048. Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401. Ilsley, W. H.; Schaaf, T. F.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3769. Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 287. Armstrong, D. R.; Clegg, W.; Colquhoun, H. M.; Daniels, J. A.; Mulvey, R. E.; Stephenson, I. R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1987**, 630.

(62) Schleyer, P. v. R.; Tidor, B.; Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Kos, A. J.; Luke, B. T.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 484.

(63) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302. Also see ref 38.

Table VI. Reaction Energies (kcal/mol) for Oligomerization, Stepwise Association, and Related Reactions of Methyllithium at Various Levels[a,b]

	MNDO	STO-3G// STO-3G	3-21G// 3-21G	6-31G	MP2/ 6-31G	6-31G+ 6d(C)	MP2/ 6-31G*	Δ(ZPE)[c]	final est[d]	energy per monomer[e]
$2CH_3Li \rightarrow (CH_3Li)_2$	-72.2	-40.0	-46.3	-41.7	-41.0	-42.6	-45.4	+1.1	-44.3	-22.2
$3CH_3Li \rightarrow (CH_3Li)_3$	-127.9	-84.5	-89.9	-80.9	-82.4	-80.2		+2.7	-79.0	-26.3
$4CH_3Li \rightarrow (CH_3Li)_4$	-207.6	-129.1	-138.0	-122.4	-128.3	-122.4		+5.4	-122.9	-30.7
$(CH_3Li)_2 + CH_3Li \rightarrow (CH_3Li)_3$	-55.7	-44.5	-43.6	-39.1	-41.4	-37.8		+1.3	-38.8	-12.9
$(CH_3Li)_3 + CH_3Li \rightarrow (CH_3Li)_4$	-79.7	-41.7	-48.1	-41.5	-45.9	-42.2		+2.6	-44.0	-11.0
$3(CH_3Li)_2 \rightarrow 2(CH_3Li)_3$	-39.2	-49.1	-41.0	-36.5	-41.7	-33.1		+1.2	-37.1	-6.2
$(CH_3Li)_4 \rightarrow 2(CH_3Li)_2$	+63.2	+46.2	+45.5	+38.9	+46.3	+37.5		-2.5	+42.4	+10.6
$3(CH_3Li)_4 \rightarrow 4(CH_3Li)_3$	+111.2	+40.5	+54.5	+43.7	+55.5	+46.3		-5.2	+52.9	+4.4
$2(CH_3Li)_4 \rightarrow (CH_3Li)_2 + 2(CH_3Li)_3$	+87.2	+43.3	+50.0	+41.3	+50.9	+41.9		-3.9	+47.6	+6.0

[a] Presented in part in ref 34. [b] Calculated by using the energies from Table I; all species in their most stable conformations. [c] Difference in zero point energies, scaled by 0.9.[50] [d] Final estimate evaluated adding the MP2 corrections to the HF results, each at the highest level employed + Δ(ZPE). [e] Using the estimates from the previous column.

nosilver complexes,[64] and benzylsodium.[65]

Table VI summarizes the oligomerization energies of methyllithium at various levels. The ab initio values are rather independent of basis set. The effect of electron correlation is small: about 2% for the dimer and trimer and 5% for the tetramer. The energy gain per monomer also is largest (-30.7 kcal/mol) for the latter, compared with only -22.2 kcal/mol for the dimer and -26.3 kcal/mol for the trimer. This helps explain why only tetramers are found experimentally in the solid state. Despite incomplete geometry optimization, the few values given in the literature for dimerization and trimerization at higher ab initio levels (basis sets better than minimal)[26,28] are comparable to ours.

MNDO always overestimates oligomerization energies by about 15 kcal/mol for the dimer and trimer and by 21 kcal/mol for the tetramer, calculated on a per monomer basis. This results from the previously mentioned overestimation of the strength of the carbon-lithium bond by MNDO and has to be considered in the discussion of such semiempirical results. The overestimation by MNDO is quite mild; however, in comparison to the early CNDO and INDO studies,[22a,b] the CH_3Li tetramerization energy was overestimated by thousands of kilocalories per mole! The more elaborate PRDDO method, applied by Graham, Richtsmeier, and Dixon[26] to these systems, also seems to provide reasonable results but favors the eight-membered ring $(CH_3Li)_4$ tetramer over the tetrahedral form.

Table VI clearly shows that aggregates lower than the tetramer are thermodynamically unfavorable for isolated methyllithium clusters. Addition of a CH_3Li monomer to the dimer and to the trimer results in energy gains of 38.8 and 44.0 kcal/mol, respectively. All possible deaggregations of the tetramer are endothermic. If dissociation occurs (which should be easier with larger groups than methyl), the data suggest that mainly the trimer should be formed. This is contrary to the experimental findings: *n*-butyllithium, e.g., exists as a dynamic equilibrium between tetramer and dimer in tetrahydrofuran.[66,67] Trimers have not been observed for any organolithium compounds, although trimeric lithium amide derivatives are known.[68]

Table VII. Enthalpies (ΔH), Entropies (ΔS), and Free Enthalpies (ΔG) of Dissociation Reactions of Methyllithium Tetramer at Various Temperatures[a]

equation	T, K	ΔH (MNDO)	ΔH (corr)[b]	ΔS	ΔG
$(CH_3Li)_4 \rightarrow 2(CH_3Li)_2$ (3)	250	63.2	42.4	63.3	26.6
	298	63.2	42.4	63.2	23.5
	350	63.1	42.3	63.0	20.2
$(CH_3Li)_4 \rightarrow {}^1/_2(CH_3Li)_2$ (4)	250	36.9	17.5	34.3	8.9
	298	37.0	17.6	34.5	7.3
	350	37.0	17.6	34.6	5.5
$(CH_3Li)_4 \rightarrow {}^1/_2(CH_3Li)_2 + (CH_3Li)_3$ (5)	250	43.5	23.8	41.5	13.4
	298	43.5	23.8	41.7	11.4
	350	43.5	23.8	41.7	9.2

[a] MNDO calculation; ΔH and ΔG in kcal/mol and ΔS in cal K^{-1} mol^{-1}. [b] Corrected using ab initio values, for details see text.

Table VIII. Enthalpies (ΔH), Entropies (ΔS), and Free Enthalpies (ΔG) of Dissociation Reactions of Solvated Methyllithium Tetramer at Various Temperatures[a]

equation ($S = NH_3$)	T, K	ΔH (MNDO)	ΔH (corr)[b]	ΔS	ΔG
$(CH_3Li{\cdot}S)_4 + 4S \rightarrow 2(CH_3Li{\cdot}S_2)_2$ (6)	250	17.1	-3.7	-79.4	16.2
	298	17.4	-3.4	-78.3	19.9
	350	17.8	-3.0	-77.1	24.0
$(CH_3Li{\cdot}S)_4 + 4S \rightarrow {}^4/_3(CH_3Li{\cdot}S_2)_3$ (7)	250	43.6	24.2	-99.5	49.1
	298	44.1	24.7	-97.7	53.8
	350	44.7	25.3	-95.9	58.8
$(CH_3Li{\cdot}S)_4 + 4S \rightarrow {}^1/_2(CH_3Li{\cdot}S_2)_2 + (CH_3Li{\cdot}S_2)_3$ (8)	250	37.0	17.3	-94.5	40.9
	298	37.4	17.7	-92.9	45.4
	350	37.9	18.2	-91.2	50.2

[a] MNDO calculation; ΔH and ΔG in kcal/mol and ΔS in cal K^{-1} mol^{-1}. [b] Corrected using ab initio values, for details see text.

For such equilibria in solution, however, entropy and solvation effects must be considered. Since the energetic differences between the various dissociation modes of the tetramer (see eq 3-5 and Table VI) are relatively small, entropy may significantly affect the equilibria. Dissociation always is favored by entropy, but eq 3 results in the formation of the greatest number of species. This also

	ΔE (kcal/mol)	
$(CH_3Li)_4 \rightarrow 2(CH_3Li)_2$	+42.4	(3)
$(CH_3Li)_4 \rightarrow {}^4/_3(CH_3Li)_3$	+17.6	(4)
$(CH_3Li)_4 \rightarrow {}^1/_2(CH_3Li)_2 + (CH_3Li)_3$	+23.8	(5)

---

(64) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1087, 1156.

(65) Schade, C.; Schleyer, P. v. R.; Dietrich, H.; Mahdi, W. *J. Am. Chem. Soc.* **1986**, *108*, 2484.

(66) (a) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. (b) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848. Also see: Fraenkel, G.; Hsu, H.; Su, B. M. In *Lithium: Current Applications in Science, Medicine, and Technology*; Bach, R. O., Ed.; Wiley: New York, 1985; Chapter 19 and references cited.

(67) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 1805. Also see: McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *J. Am. Chem. Soc.* **1985**, *107*, 1810.

(68) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229. Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285. Also see ref 38.

holds for solvation effects, since the tetramer has only one but both the dimer and trimer have two solvation sites per lithium (eq 6–8). We have attempted to evaluate this

$$(CH_3Li{\cdot}S)_4 + 4S \rightarrow 2(CH_3Li{\cdot}S_2)_2 \qquad (6)$$

$$(CH_3Li{\cdot}S)_4 + 4S \rightarrow {}^4/_3(CH_3Li{\cdot}S_2)_3 \qquad (7)$$

$$(CH_3Li{\cdot}S)_4 + 4S \rightarrow {}^1/_2(CH_3Li{\cdot}S_2)_2 + (CH_3Li{\cdot}S_2)_3 \qquad (8)$$

$$S = \text{solvent molecule}$$

situation by means of semiempirical MNDO calculations including entropy and solvation effects. Ammonia has been chosen as a model solvent. Thermodynamic functions were obtained by the standard statistical formulae contained in the MOPAC and AMPAC program packages.[49] Though most of the molecules considered had some very low-lying vibrational frequencies (most of them being internal rotations) which cause errors in the *absolute* values, *relative* values and trends should be reliable. As mentioned before, MNDO association energies of organolithium compounds are seriously overestimated, whereas solvation energies are given well.[69] Thus, the procedure applied was as follows: Changes in thermodynamic functions (enthalpy ΔH, entropy ΔS) were calculated by using MNDO. ΔH values for reactions involving any association or dissociation were then corrected by using the ab initio final estimates for the corresponding solvent-free reactions leading to changes in free enthalpy, ΔG. The results for various temperatures are given in Tables VII and VIII.

As expected, all *solvent-free* dissociation modes are more favorable at higher temperatures (Table VII). Formation of the trimer (eq 4) is most favorable ($\Delta G = +7.3$ kcal/mol at room temperature). However, when solvation is considered (eq 6–8), the situation is quite different. All dissociation modes are favored with *decreasing* temperature (Table VIII). This clearly is an entropy effect. Whereas the entropy term for eq 3–5 is positive (34–63 cal K^{-1} mol^{-1}) and nearly temperature independent for each of the dissociation modes, it is large and negative (−100 to −77 cal K^{-1} mol^{-1}) and somewhat temperature dependent for eq 6–8. This results mainly from a loss of translational freedom since additional solvent molecules are bound. Now formation of the *dimer* is by far the most favorable reaction ($\Delta G = +19.9$ kcal/mol at room temperature, compared with about +50 kcal/mol for the other reactions). The main factor in the competition between dimers and trimers is the energy term: the transformation of three dimers into two trimers is *exothermic* by −37.1 kcal/mol in the gas phase (Table VI) whereas the corresponding reaction with solvent is *endothermic* by 42.2 kcal/mol. Our results explain the experimental findings nicely: alkyllithium trimers have never been found, whereas in 1983 Seebach et al.[66a] first reported the observation of an equilibrium between tetramers and dimers of butyllithium in tetrahydrofuran solution by means of ^{13}C NMR and $^{13}C,^{6}Li$ coupling. At the same time, the corresponding process for lithium enolates has been observed by Jackman and DeBrosse.[70] Both groups provided the entropy explanation for the higher concentrations of dimer upon cooling. Subsequently, many additional organolithium tetramer–dimer equilibria have been observed.[18b] In 1985, the thermodynamic parameters for the butyllithium reaction were measured by Seebach et al.[66b] and by McGarrity et al.[67] using ^1H NMR. The small change in enthalpy for the deaggregation reaction, −3.6 to −1.5 kcal/mol,[66,67] is well-reproduced by our calculations (−3.7 kcal/mol at 250 K, Table VIII). Larger deviations occur for the entropy term: Seebach et al.[66] give −26.3 (NMR integration) and −18.8 cal K^{-1} mol^{-1} (NMR line-shape analysis) and McGarrity et al.[67] −13.9 cal K^{-1} mol^{-1}. Our calculated value (−79.4 cal K^{-1} mol^{-1} at 250 K) is much too negative. However, dimers and trimers are indicated not to be fully coordinated by two solvent molecules per lithium, even at low temperatures. In the case of $(CH_3Li)_2$, ΔG for the first solvation step (one NH_3 per lithium) is −15.6 and for the second (two NH_3s per lithium) +8.6 kcal/mol at 250 K. A fully solvated trimer is not likely to even exist at all ($\Delta G = +30.3$ kcal/mol). Thus less than four solvent molecules will be bound additionally in reaction 6, bringing the entropy term closer to the experimental value. However, these results should not be interpreted too quantitatively, since this is a rather crude model: semiempirical reaction enthalpies at higher temperatures have been corrected by ab initio energies corresponding to 0 K. No conversion of the latter to higher temperatures (temperature dependence of vibrational populations etc.) or to enthalpies (pV term) have been made. The assumption that differences in aggregation energies are the same for solvated and unsolvated species may not be strictly valid. Also, the calculated reactions refer to isolated "supermolecules" in the gas phase, whereas the experimental values have been measured in condensed phase by using different alkyllithiums and solvents. Some conclusions, however, seem to be rather reliable: if simple alkyllithiums (tetramers) in donor solvents dissociate at all, dimers will be formed. Neither trimers nor monomers are to be expected. Recently, McGarrity et al.[67] have demonstrated that in the addition to ketones butyllithium dimers are the reactive species in tetrahydrofuran solution. No evidence could be obtained for even very low concentrations of monomers.

With use of a cavity model, Sapse and Jain[71] studied the effect of solvent on monomer–dimer equilibria of lithium compounds. As the authors state, "the continuum model is improved by considering the local interactions", e.g., their calculated solvation energy of CH_3Li in water (−3.9 kcal/mol)[71] is far exceeded by the interaction energy of CH_3Li with a single H_2O molecule (−18.0 kcal/mol).[69] However, the cavity model may be useful to improve results obtained by a "supermolecule" approach.

Analysis of the Bonding in Methyllithium Oligomers. Natural population analysis[53a] of the methyllithium oligomers (Table IX) indicates that they are slightly more ionic than the monomer. As each carbon atom in the oligomers has two or three lithium nearest neighbors, the C–Li bonding is highly delocalized, in contrast to that in the monomer. The most localized description of the C–Li bonding is obtained by first forming natural hybrid orbitals (NHOs)[53b] for the carbon lone pairs (and also the C–H bonds) and then allowing these to delocalize onto the lithium orbitals by the natural localized molecular orbital (NLMO)[53c] procedure. One thus obtains doubly occupied NLMOs describing the bonding of each carbon lone pair with the positively charged Li_n core. These carbon lone pair NHOs are characterized in Table IX by their occupancy, % p character, and orbital energy. Also given are the orbital energies of the corresponding NLMOs for the delocalized carbon lone pairs. Though the lithium charges

---

(69) Kaufmann, E.; Gose, J.; Schleyer, P. v. R., manuscript in preparation. Also see: Kaufmann, E.; Tidor, B.; Schleyer, P. v. R. *J. Comput. Chem.* **1986**, *7*, 334.

(70) Jackman, L. M.; DeBrosse, C. W. *J. Am. Chem. Soc.* **1983**, *105*, 4177.

(71) Sapse, A. M.; Jain, D. C. *J. Phys. Chem.* **1987**, *91*, 3923.

Table IX. Bonding Analysis of Methyllithium Oligomers[a]

number of monomers	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 4$	$n = 4$
symmetry of oligomer	C_{3v}	C_{2h}	C_{3h}	C_{4h}	T_d, stagg	T_d, ecl
natural charges						
H	+0.184	+0.188 (2) +0.194 (4)	+0.197 (3) +0.200 (6)	+0.202	+0.205	+0.192
C	−1.362	−1.437	−1.426	−1.418	−1.484	−1.430
Li	+0.811	+0.860	+0.829	+0.811	+0.869	+0.855
carbon lone pair						
NHO occupancy	1.817	1.870	1.840	1.820	1.882	1.873
NHO % p char	81.3	79.2	78.6	78.3	78.0	77.8
ϵ_{NHO}, au	−0.278	−0.334	−0.341	−0.343	−0.359	−0.357
ϵ_{NLMO}, au	−0.326	−0.383	−0.398	−0.403	−0.411	−0.413
ϵ_{HOMO}(av),[b] au	−0.272	−0.321	−0.335	−0.341	−0.339	−0.345
agostic interactions						
$\Delta E_{del}(\sigma_{CH} \rightarrow n_{Li})$[c]	−1.6	−10.1	−20.3	−29.4	−32.0	−44.0

[a] Analysis of the 3-21G//3-21G wave functions for $(CH_3Li)_n$; see the text. [b] Average of the top n MO eigenvalues. [c] Total energy change due to all $\sigma_{CH} \rightarrow n_{Li}$ delocalization, by NBO Fock maatrix deletion method,[74] in kcal/mol.

do not change smoothly with n, there is a steady decrease of the % p character and of the NHO and NLMO orbital energies of the carbon lone pairs with oligomerization. In addition, the lone-pair energies are lower for the more stable T_d than for the less stable C_{4h} tetramers. Similar trends are also seen in the HOMO energies, though these are somewhat masked by the effects of symmetry splitting and of mixing with lower energy C–H bond LMOs. The decrease of the H–C–H angles from 106.9° in the monomer to 103.9° in the T_d eclipsed tetramer is consistent with the decrease in the % p character of the carbon lone pairs (and consequent increase in p character of C–H bond hybrids) seen in Table IX. Guest et al.[22b] have previously computed LMOs for the tetramer, presenting plots of carbon lone-pair LMOs. On the basis of Mulliken population analysis, they also found a high amount of p character (81%) in the carbon lone pair.

Though the primary CH_3–Li covalent interactions in the methyllithium oligomers are those involving the carbon lone pairs, delocalization from the C–H bonds onto the lithium atoms occurs as well. This σ_{CH}–Li interaction[72] is the organolithium form of the "agostic interaction", which has generally only been discussed in relation to transition-metal complexes of hydrocarbons.[73] This agostic interaction is negligible in CH_3Li monomer but becomes much stronger with oligomerization, reaching peak strength in the T_d eclipsed tetramer. Due to lithium clustering within the oligomer, the Li–C–H angles are greatly reduced as are the Li–H distances. This makes the interactions geometrically more favorable. Indeed, in the T_d eclipsed tetramer, the Li–H distance is hardly longer than the Li–C distance (2.240 vs 2.236 Å). Various fine details of the geometries of the oligomers can be explained on the basis of the drive toward maximization of agostic stabilization. Where the hydrogens are not symmetry-equivalent (i.e., in the C_{nh} oligomers), the C–H bonds that are closest to a lithium atom are 0.001–0.004 Å longer than the other C–H bonds, and the C–H bonds in the T_d eclipsed tetramer are 0.008 Å longer than those in CH_3Li. Additionally, the nonequivalence of the two nearest-neighbor C–Li distances in the C_{nh} oligomers (and the associated angular distortions of the C_nLi_n framework) could have their origin in the tilting of the methyl groups to reduce in-plane H–C–Li angles and H–Li distances. As seen from Table IX, the unique, in-plane hydrogen atoms in the C_{nh} oligomers have natural charges that are less positive than the nonunique, out-of-plane hydrogens. This is due to the fact that the C–H bond orbitals for the in-plane hydrogens are less polar toward carbon. This subtle effect, seen most strongly in the C_{2h} dimer and almost not at all in the C_{4h} tetramer, indicates that the agostic interaction induces a small polarization of the C–H bond toward hydrogen, making the σ_{CH} bond more electron rich at the hydrogen and a better donor.

The energetic significance of the agostic interactions can be judged by second-order perturbative energy estimates based on σ_{CH}–n_{Li} NBO Fock matrix elements,[74] where n_{Li} is the lithium valence NHO of mainly 2s character. For the dominant nearest-neighbor agostic interactions, these estimates range from −0.8 kcal/mol in the monomer to −4.6 kcal/mol in the T_d eclipsed tetramer, per σ_{CH}–n_{Li} interaction. More reliable energetic estimates are obtainable through the NBO Fock matrix deletion procedure,[74] setting all of the σ_{CH}–n_{Li} NBO Fock matrix elements to zero and reevaluating the energy. The agostic stabilization energies obtained with this deletion procedure are presented in Table IX. The strongest stabilization is again in the T_d eclipsed tetramer with a total of 44 kcal/mol, or 3.7 kcal/mol per C–H bond, slightly less than the above second-order estimate. In the T_d staggered tetramer, the σ_{CH}–n_{Li} overlap is weaker and the agostic stabilization is estimated to be only 32 kcal/mol. Through the rotation of the methyl groups, 12 kcal/mol of agostic stabilization is lost, or 1 kcal/mol per C–H bond. Thus, in the absence of agostic interactions, the T_d staggered tetramer becomes almost 10 kcal/mol more stable than the eclipsed form at the 3-21G level.

In addition to exerting an important influence on oligomer conformation, agostic interactions also favor higher degrees of oligomerization, as seen in Table IX. At the 3-21G//3-21G level, agostic interactions are estimated to contribute 36 kcal/mol to the total 138 kcal/mol tetramerization energy of methyllithium. The agostic stabilization and the more important purely electrostatic stabilization of the σ_{CH} electrons in the positive field of the lithium cluster serve to lower the σ_{CH} orbital energies in the oligomers to values much closer to those in CH_4. The σ_{CH} NLMO energies in CH_3Li, $(CH_3Li)_4$ T_d eclipsed, and CH_4 at the 3-21G level are −0.600, −0.657, and −0.680 au, respectively. Thus, the destabilization of the σ_{CH} orbitals in CH_3Li due to the anionic character of the carbon dis-

---

(72) For both experimental and further theoretical evidence for Li–H agostic interactions, see: Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. v. R. *Angew. Chem.* **1986**, *98*, 1130; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1103. Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970.

(73) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

(74) See, e.g.: Curtiss, L. A.; Pochatko, D. J.; Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *82*, 2679.

Table X. MNDO Heats of Formation (kcal/mol), Total Energies (au), and Relative Energies (kcal/mol, in Parentheses) of Tetrameric Clusters in Different Conformations with and without Solvent

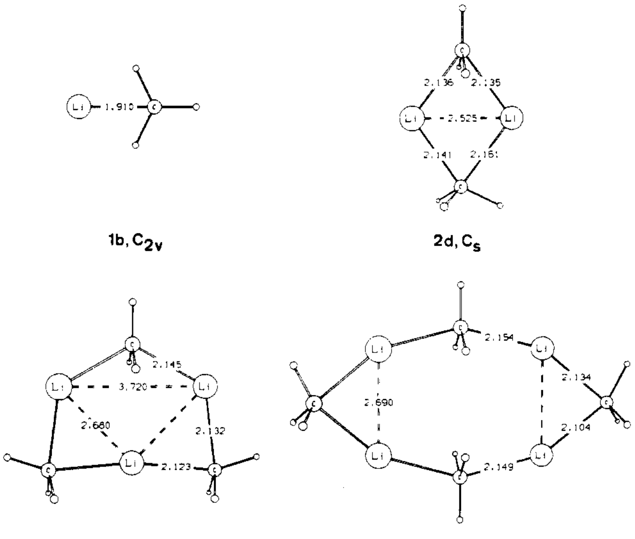
cluster $(R^1Li{\cdot}S)_3(R^2Li{\cdot}S)$				conformatn				
R^1	R^2	S	point group	R^1	R^2	MNDO	STO-3G//STO-3G	3-21G//3-21G
H	CH_3	none	C_{3v}		ecl	−143.3 (0.0)	−70.215 80 (0.0)	−70.761 03 (0.0)
			C_{3v}		stagg	−141.6 (1.7)	−70.208 31 (4.7)	−70.759 55 (0.9)
H	CH_3	NH_3	C_{3v}		ecl	−203.1 (0.0)		
			C_{3v}		stagg	−202.9 (0.2)		
H	C_2H_5	none	C_s		ecl	−147.6 (0.0)		−109.571 84 (0.0)
			C_s		stagg	−145.3 (2.3)		−109.568 24 (2.3)
H	C_2H_5	NH_3	C_s		ecl	−203.8 (0.3)		
			C_s		stagg	−204.1 (0.0)		
CH_3	CH_3	none	T_d	ecl	ecl	−213.2 (0.0)	−185.887 39 (0.0)	
			T_d	stagg	stagg	−205.4 (7.8)	−185.858 30 (18.3)	
			C_{3v}	ecl	stagg	−211.3 (1.9)	−185.880 33 (4.4)	
CH_3	CH_3	NH_3	T_d	ecl	ecl	−263.0 (0.8)		
			T_d	stagg	stagg	−263.8 (0.0)		
			C_{3v}	stagg	ecl	−262.6 (1.2)		
CH_3	C_2H_5	none	C_s	ecl	ecl	−217.3 (0.0)		
			C_s	ecl	stagg	−214.7 (2.6)		
CH_3	C_2H_5	NH_3	C_s	ecl	ecl	−261.5 (1.2)		
			C_s	ecl	stagg	−262.7 (0.0)		

appears to a large extent upon oligomerization.

Conformational Studies. As has been mentioned before, the methyl groups in crystalline methyllithium[7] adopt a *staggered* conformation with respect to the Li_3 face of the tetrahedral cluster, due to the coordination of the lithium atoms with methyl groups from neighboring clusters. Since the distance between the Li and the CH_3 group of the next-nearest neighbor cluster has been found to be only 2.52 Å,[7] agostic interactions will certainly play a role in this $Li{\cdots}H_3C$ bonding. In contrast, all calculations of $(CH_3Li)_4$ predict the *eclipsed* conformation to be more stable.[23,24] Our best estimate for the energy difference is 6.9 kcal/mol (Table II), or 1.7 kcal/mol per methyl group. The latter value should be a good estimate for the rotation barrier if all the methyl groups rotate independently. To check this further including solvent effects, we have carried out model calculations of species $(R^1Li{\cdot}S)_3(R^2Li{\cdot}S)$ (S = solvent) with the substituents R^1 and R^2 in different conformations. Table X shows indeed that the rotation of one methyl group in $(CH_3Li)_4$ costs only a fourth of the energy required to rotate all four methyl groups simultaneously. The STO-3G minimal basis relative energies are inaccurate (see also Table II), whereas the MNDO results are comparable to those obtained at the higher ab initio levels. The conformational preferences of the larger ethyl group are the same as those for methyl. Whereas in the X-ray structure of $(C_2H_5Li)_4$ it adopts a *staggered* conformation with respect to the Li_3 face,[8] calculations (Table X) show the *eclipsed* conformation to be the preferred one in isolated (gas phase) tetramers. The rotation barrier of the ethyl group, estimated by using R^1 = H at the ab initio level, appears to be about twice as high (ca. 2 kcal/mol) as that for methyl. Nevertheless, all the energy differences are small.

Solvation reverses the relative stabilities of eclipsed and staggered conformations. At the MNDO level, the $(CH_3Li)_4$ cluster solvated by one ammonia molecule per lithium is 0.8 kcal/mol more stable in the staggered conformation. Though the absolute values given here are not expected to be very accurate, the trend is obvious: The staggered conformation of the $(CH_3Li)_4$ units found in the crystal[7] is due to a packing effect, since each lithium is "solvated" by a neighboring cluster. The Li–H interactions in the eclipsed conformation are overcome by the sterically more favorable staggered orientation.

Methyl Inversion in Methyllithium. As has been mentioned before, primary alkyllithiums undergo facile stereomutation at the α-carbon. The activation energies for inversion are known experimentally to be unusually low (about 15 kcal/mol); the kinetics are first-order with a very small activation entropy.[36,37] In 1978, it was shown by 4-31G//STO-3G ab initio calculations[24] that the rather high barrier in monomeric methyllithium (the planar C_{2v} transition structure **1b** (Figure 3) was calculated to lie about 42 kcal/mol above the C_{3v} minimum **1a**) is reduced considerably upon dimerization (to about 23 kcal/mol).[24] We have now reinvestigated this problem at higher levels including electron correlation and extended it to the trimer and the tetramer. The recent computer program developments in applied theoretical chemistry[34] enabled us to locate the dimeric transition structure **2d** at the 3-21G and 6-31G* levels. It is characterized by one negative eigenvalue of the 3-21G force constant matrix and is very similar to that originally proposed in 1978.[24] The inverting methyl group is almost planar. Thus, for computational convenience, it seems reasonable to approximate the transition structures by models having planar methyl groups on symmetry grounds. The structures we considered for the trimer and tetramer are the C_{2v} species **3c** and **4d**, having one and two planar methyl groups, respectively (Figure 3). The orientation of the remaining methyls is not expected to change relative energies significantly (compare dimers



1b, C_{2v} **2d**, C_s

3c, C_{2v} **4d**, C_{2v}

Figure 3. Models for the transition structures for methyl group inversion in methyllithium oligomers (3-21G basis, distances in Å).

Table XI. Enthalpies (ΔH), Entropies (ΔS), and Free Enthalpies (ΔG) of Methyl Inversion Reactions of Methyllithium Oligomers at 298 K[a]

species (S = NH_3)	ΔH (MNDO)	ΔH (corr)[b]	ΔS	ΔG
$(CH_3Li)_2$	38.7	16.7	−4.8	18.1
$(CH_3Li{\cdot}S)_2$	35.8	13.8	1.2	13.5
$(CH_3Li{\cdot}S_2)_2$	34.4	12.4	−2.4	13.1
$(CH_3Li)_3$	27.0	13.3	−5.4	14.9
$(CH_3Li{\cdot}S)_3$	19.5	5.8	−2.9	6.7
$(CH_3Li{\cdot}S_2)_3$[c]	17.1	3.4		
$(CH_3Li)_4$[d]	38.5	14.3		
$(CH_3Li{\cdot}S)_4$[d]	36.4	12.2		
$(CH_3Li{\cdot}S_2)_4$[c–e]	36.8	12.6		

[a] MNDO calculation; ΔH and ΔG in kcal/mol, ΔS in cal K^{-1} mol^{-1}. [b] Corrected by using ab initio values, for details see text. [c] Second solvation shell not bound. [d] Actually calculated with two planar methyl groups in the transition structure; the energies given were divided by 2. [e] Corresponds to the inversion reaction with change in extent of solvation: $(CH_3Li{\cdot}S)_4$ (tetrahedral) + 4S → $(CH_3Li{\cdot}S_2)_4$ (eight-membered ring).

2a and **2b**). Indeed, **3c** is a true transition structure at the MNDO level (one imaginary frequency). In the case of **4d**, half of the relative energy is expected to be an upper limit for the inversion barrier. Thus, our final estimates (Table II) for the inversion barriers for a methyl group in methyllithium oligomers are 30.9 (monomer), 16.7 (dimer), 13.3 (trimer), and 14.3 kcal/mol (tetramer). The latter value agrees very well with those determined experimentally,[36,37] and our mechanism for the inversion seems to be a good model. However, experimental inversion barriers have been measured in solution,[36,37] and solvation of the lithium species involved may alter the mechanism, e.g., although unlikely, leading to free carbanions, or reducing the barrier (tetrahedral $(CH_3Li)_4$ has one solvation site per lithium, but two may be expected to be present in the eight-membered ring). Therefore we modeled the inversion process in solution using MNDO. The gas-phase transition structure models **2d**, **3c**, and **4d** were solvated with ammonia. In analogy to the study of equilibria between different oligomers, the MNDO data were corrected by using the ab initio final estimates (the MNDO barriers are too high by 13–24 kcal/mol per inverting methyl group, see Table II). The results are summarized in Table XI. Solvation does reduce the barriers somewhat, e.g., by about 3 kcal/mol in the dimer and by about 2 kcal/mol in the tetramer, if they are solvated by one ammonia molecule per lithium. However, the solvation energies are not large enough to disrupt the aggregate structures. With respect to the experimental inversion barriers, the very low activation energy in the trimer (5.8 kcal/mol) is of no significance, since, as has been previously stated, trimers are not present in solution. A further lowering of the barriers due to a second ammonia molecule per lithium is only observed for the dimer (to 12.4 kcal/mol, Table XI). The additional solvent is *not bound* in both the trimeric (ΔH = +7.2 kcal/mol) and in the eight-membered ring tetrameric (ΔH = +0.7 kcal/mol) transition-state models, although (as noted above) both appear to have two solvation sites per lithium in contrast to the tetrahedral $(CH_3Li)_4$, which has only one solvation site per lithium (see previous discussion of equilibria). A more extensive study of the transition states for methyl inversion including entropy effects was carried out for the dimers and (partly) the trimers. Only the data at 298 K are given in Table XI, since all inversion processes are nearly temperature independent; ΔH and ΔG vary only by 0.2 and 0.5 kcal/mol, respectively, in the temperature range 250–350 K. This is mainly due to the small entropy contributions (−5 to 1 cal K^{-1} mol^{-1}), which accord with those determined experimentally.[36,37] Hence, *inversion does not take place by dissociation–recombination*, as was once suggested,[36] *nor via free carbanions*. Instead, inversion occurs within the aggregate[37] and involves polycoordinate carbon species with trigonal-bipyramidal symmetry and the critical substituents in a plane.[75]

Acknowledgment. This paper is dedicated to Prof. H. Dietrich, who established the first tetrahedral structure of an alkyllithium tetramer by X-ray analysis. Support was provided by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Convex Computer Corp. We also thank Prof. E. Weiss and Dr. W. R. Winchester for discussions.

Registry No. **1a**, 917-54-4; **2a**, 74309-22-1; **2c**, 113859-42-0; **3a**, 74316-42-0; **3b**, 113859-43-1; **4a**, 20670-26-2; **4a**·$4NH_3$, 113859-47-5; **4c**, 74309-23-2; $(HLi)_3(CH_3Li)$, 113859-44-2; $(HLi{\cdot}NH_3)_3(CH_3Li{\cdot}NH_3)$, 113859-45-3; $(HLi)_3(C_2H_5Li)$, 113859-46-4; $(HLi{\cdot}NH_3)_3(C_2H_5Li{\cdot}NH_3)$, 113892-39-0; $(CH_3Li)_3(C_2H_5Li)$, 113859-48-6; $(CH_3Li{\cdot}NH_3)_3(C_2H_5Li{\cdot}NH_3)$, 113859-49-7; NH_3, 7664-41-7.

Supplementary Material Available: Full geometry information in the form of archive entries or **Z** matrices for all the species calculated ab initio (8 pages). Ordering information is given on any current masthead page.

---

(75) See ref 65 and references cited. Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527.