The chemistry of
organolithium compounds
Part 1

Edited by

ZVI RAPPOPORT
The Hebrew University, Jerusalem

ILAN MAREK
Technion-Israel Institute of Technology, Haifa

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John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester,
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Eitan, Alon and **Naomi**

and

Haya, Efraim and **Rivka**

Contributing authors

Manfred Braun	Institut für Organische Chemie und Makromolekulare Chemie, Universität Düsseldorf, D-40225 Düsseldorf, Germany
Marvin Charton	Chemistry Department, School of Liberal Arts and Sciences, Pratt Institute, Brooklyn, NewYork 11205, USA
Fabrice Chemla	Laboratoire de Chimie Organique, Université Pierre et Marie Curie, Tour 44-45 2ème étage, Bte 183, 4 Place Jussieu, 75252 Paris Cedex 05, France
Guido Christoph	Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster, Germany
Jonathan Clayden	Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
Iain Coldham	School of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD, UK
Chagit Denekamp	Department of Chemistry, Technion–Israel Institute of Technology, Technion City, 32000 Haifa, Israel
Robert E. Gawley	Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA
G. Gopakumar	School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad 500 046, Andhra Pradesh, India
Harald Günther	University of Siegen, Fachbereich 8, OCII, D-57068 Siegen, Germany
Dieter Hoppe	Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster, Germany
Eluvathingal D. Jemmis	School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad 500 046, Andhra Pradesh, India
Dan Johnels	Department of Chemistry/Organic Chemistry, Umeå University, SE-901 87 Umeå, Sweden
Wolfgang Kiefer	Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Frédéric Leroux	Laboratoire de stéréochimie, Université Louis Pasteur (ECPM), 25 rue Becquerel, F-67087 Strasbourg, France

Joel F. Liebman	Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, 1000 Hilltop Circle, Baltimore, Maryland 21250, USA
Ilan Marek	Department of Chemistry and Institute of Catalysis, Science and Technology, Technion-Israel Institute of Technology, Technion City, 32000 Haifa, Israel
I. Pavel	Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Daniel Schildbach	Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Manfred Schlosser	Institute of Molecular and Biological Chemistry, Swiss Federal Institute of Technology, CH-1015, Lausanne, Switzerland
Suzanne W. Slayden	Department of Chemistry, George Mason University, 4400 University Drive, Fairfax, Virginia 22030, USA
Dietmar Stalke	Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Thomas Stey	Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Carsten Strohmann	Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
K. Tomioka	Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606–8501, Japan
Katsuhiko Tomooka	Department of Applied Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152–8552, Japan
Emmanuel Vrancken	Laboratoire de Chimie Organique, Université Pierre et Marie Curie, Tour 44-45 2ème étage, Bte 183, 4 Place Jussieu, F-75252 Paris Cedex 05, France
K. Yamada	Graduate School of Pharmaceutical Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606–8501, Japan
Hiroshi Yamataka	Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567–0047, Japan
Miguel Yus	Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain
Jacob Zabicky	Institutes for Applied Research, Ben-Gurion University of the Negev, P. O. Box 653, Beer-Sheva 84105, Israel
Elinor Zohar	Department of Chemistry and Institute of Catalysis, Science and Technology, Technion—Israel Institute of Technology, Technion City, 32000 Haifa, Israel

Foreword

This is another volume in 'The Chemistry of Functional Groups' series which deals with organometallic derivatives. We have assembled the remarkable recent achievements in the synthesis, structure, synthetic uses and spectroscopy of organic lithium derivatives which are in daily use in the organic chemist's laboratory.

The two parts of the present volume contain 18 chapters written by experts from 10 countries. They include chapters on new developments, since Sapse and Schleyer's *Lithium chemistry* published in 1995, dealing with theoretical aspects, structural chemistry, thermochemistry, various spectroscopic characteristics such as solid state NMR and vibrational spectroscopy, and gas phase chemistry, of organolithium compounds. Mechanistically oriented chapters deal with directing and activating effects of organolithium derivatives and the mechanism of their additions to double bonds. There are chapters on analysis, as well as on rearrangements of organolithium compounds and on specific classes such as polylithium compounds, lithium carbenoids and α-amino-organolithiums.

Several chapters deal with the synthesis of and the synthetic applications of organolithium compounds such as orthometallation, arene catalysed lithiation, addition to carbon–carbon double bonds, their reaction with oxiranes, and asymmetric deprotonation with lithium (-)-sparteine. We gratefully acknowledge the contributions of all the authors of these chapters.

Three promised chapters on the dynamic behaviour of organolithium compounds, on chiral alkyllithium amides in asymmetric synthesis and on the intramolecular carbolithiation reaction were not delivered. Although some material related to the first of these two chapters appear partially in other chapters, we hope that the missing chapters will appear in a future volume.

The literature coverage is mostly up to mid or late 2002, and several chapters contain references from 2003.

We will be grateful to readers who draw our attention to any mistakes in the present volume, or to omissions and new topics which deserve to be included in a future volume on organolithium compounds.

Jerusalem and Haifa
September 2003

ZVI RAPPOPORT
ILAN MAREK

The Chemistry of Functional Groups
Preface to the series

The series 'The Chemistry of Functional Groups' was originally planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the preparation, properties and reactions of the functional group treated and on the effects which it exerts both in the immediate vicinity of the group in question and in the whole molecule.

A voluntary restriction on the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series and in textbooks (i.e. in books which are usually found in the chemical libraries of most universities and research institutes), should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the topic. Therefore each of the authors is asked not to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced postgraduate level.

It is realized that no plan can be devised for a volume that would give a complete coverage of the field with no overlap between chapters, while at the same time preserving the readability of the text. The Editors set themselves the goal of attaining reasonable coverage with moderate overlap, with a minimum of cross-references between the chapters. In this manner, sufficient freedom is given to the authors to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter deals with the general and theoretical aspects of the group.

(b) Chapters discuss the characterization and characteristics of the functional groups, i.e. qualitative and quantitative methods of determination including chemical and physical methods, MS, UV, IR, NMR, ESR and PES—as well as activating and directive effects exerted by the group, and its basicity, acidity and complex-forming ability.

(c) One or more chapters deal with the formation of the functional group in question, either from other groups already present in the molecule or by introducing the new group directly or indirectly. This is usually followed by a description of the synthetic uses of the group, including its reactions, transformations and rearrangements.

(d) Additional chapters deal with special topics such as electrochemistry, photochemistry, radiation chemistry, thermochemistry, syntheses and uses of isotopically labelled compounds, as well as with biochemistry, pharmacology and toxicology. Whenever applicable, unique chapters relevant only to single functional groups are also included (e.g. 'Polyethers', 'Tetraaminoethylenes' or 'Siloxanes').

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the authors and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, some volumes may be published without giving consideration to the originally planned logical order of the chapters.

Since the beginning of the Series in 1964, two main developments have occurred. The first of these is the publication of supplementary volumes which contain material relating to several kindred functional groups (Supplements A, B, C, D, E, F and S). The second ramification is the publication of a series of 'Updates', which contain in each volume selected and related chapters, reprinted in the original form in which they were published, together with an extensive updating of the subjects, if possible, by the authors of the original chapters. A complete list of all above mentioned volumes is available from the publisher. Unfortunately, the publication of the 'Updates' has been discontinued for economic reasons.

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editors.

The publication of this series would never have been started, let alone continued, without the support of many persons in Israel and overseas, including colleagues, friends and family. The efficient and patient co-operation of staff-members of the publisher also rendered us invaluable aid. Our sincere thanks are due to all of them.

The Hebrew University SAUL PATAI
Jerusalem, Israel ZVI RAPPOPORT

Sadly, Saul Patai who founded 'The Chemistry of Functional Groups' series died in 1998, just after we started to work on the 100th volume of the series. As a long-term collaborator and co-editor of many volumes of the series, I undertook the editorship and I plan to continue editing the series along the same lines that served for the preceeding volumes. I hope that the continuing series will be a living memorial to its founder.

The Hebrew University ZVI RAPPOPORT
Jerusalem, Israel
May 2000

Contents

List of abbreviations used

Ac	acetyl (MeCO)
acac	acetylacetone
Ad	adamantyl
AIBN	azoisobutyronitrile
Alk	alkyl
All	allyl
An	anisyl
Ar	aryl
Bn	benzyl
Bz	benzoyl (C_6H_5CO)
Bu	butyl (C_4H_9)
CD	circular dichroism
CI	chemical ionization
CIDNP	chemically induced dynamic nuclear polarization
CNDO	complete neglect of differential overlap
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAH	diisobutylaluminium hydride
DME	1,2-dimethoxyethane
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulphoxide
ee	enantiomeric excess
EI	electron impact
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance
Et	ethyl
eV	electron volt

Fc	ferrocenyl
FD	field desorption
FI	field ionization
FT	Fourier transform
Fu	furyl(OC_4H_3)
GLC	gas liquid chromatography
Hex	hexyl (C_6H_{13})
c-Hex	cyclohexyl (c-C_6H_{11})
HMPA	hexamethylphosphortriamide
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
i-	iso
ICR	ion cyclotron resonance
Ip	ionization potential
IR	infrared
LAH	lithium aluminium hydride
LCAO	linear combination of atomic orbitals
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
M	metal
M	parent molecule
MCPBA	*m*-chloroperbenzoic acid
Me	methyl
MNDO	modified neglect of diatomic overlap
MS	mass spectrum
n	normal
Naph	naphthyl
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NMR	nuclear magnetic resonance
Pen	pentyl (C_5H_{11})
Ph	phenyl
Pip	piperidyl($C_5H_{10}N$)
ppm	parts per million
Pr	propyl (C_3H_7)
PTC	phase transfer catalysis or phase transfer conditions
Py, Pyr	pyridyl (C_5H_4N)

R	any radical
RT	room temperature
s-	secondary
SET	single electron transfer
SOMO	singly occupied molecular orbital
t-	tertiary
TCNE	tetracyanoethylene
TFA	trifluoroacetic acid
THF	tetrahydrofuran
Thi	thienyl (SC_4H_3)
TLC	thin layer chromatography
TMEDA	tetramethylethylene diamine
TMS	trimethylsilyl or tetramethylsilane
Tol	tolyl (MeC_6H_4)
Tos or Ts	tosyl (*p*-toluenesulphonyl)
Trityl	triphenylmethyl (Ph_3C)
Xyl	xylyl($Me_2C_6H_3$)

In addition, entries in the ‘List of Radical Names’ in *IUPAC Nomenclature of Organic Chemistry*, 1979 Edition, Pergamon Press, Oxford, 1979, p. 305–322, will also be used in their unabbreviated forms, both in the text and in formulae instead of explicitly drawn structures.

CHAPTER **1**

Theoretical studies in organolithium chemistry

ELUVATHINGAL D. JEMMIS and G. GOPAKUMAR

School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad 500 046, Andhra Pradesh, India
e-mail: jemmis@uohyd.ernet.in

I. INTRODUCTION

With their versatile structure, bonding and reactions, organolithium compounds continue to fascinate chemists. Tremendous progress has been made in each of these areas during the last few years. Theoretical studies have played an important role in these developments. Several reviews had appeared on the contribution of theoretical methods in organolithium compounds[1,2]. Wave-function-based quantum mechanical methods at various levels continue to be used in these studies; theoretical studies based on Density Functional Theory

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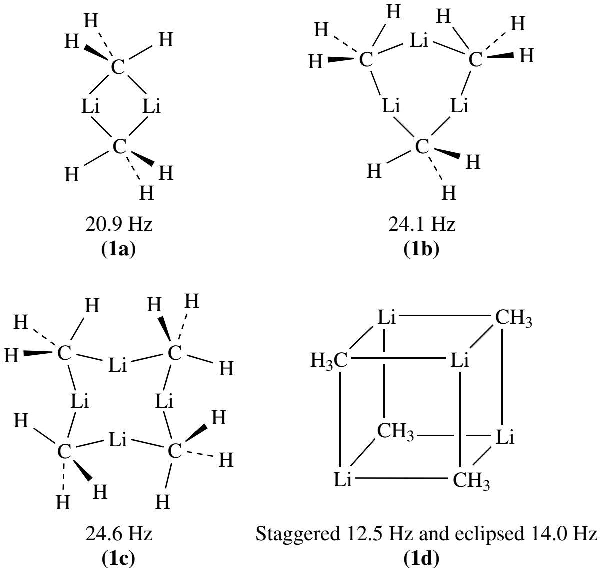
Edited by Z. Rappoport and I. Marek

(DFT) have also become popular in recent years. A major review on theoretical studies in organolithium compounds was published in 1995 by Streitwieser, Bachrach and Schleyer[2]. We concentrate here on publications that have appeared since then. During these years considerable progress has been made in the application of theoretical methods to the chemistry of organolithium compounds at various levels of sophistication depending on the problem. Attempts have been made to further delineate the nature of C−Li bonding. Semiempirical calculations with the inclusion of solvent effects through various approximations have been used to study larger systems. Reactions have been modeled in the gas phase. Mechanistic details of several reactions have been studied theoretically. We discuss the developments in the nature of the C−Li bonding first. Theoretical studies on the structure and energetics, reactions and some applications involving NMR parameters are discussed in subsequent sections.

II. THE NATURE OF THE C−Li BOND

The nature of C−Li bond is still a dilemma for chemists due to the unusual behavior of the bond in different compounds. Although the electronegativity difference suggests the carbon−lithium bond to be essentially ionic, the solubility of some organolithium compounds in nonpolar solvents such as benzene makes the problem more complex[3]. The nature of the C−Li bond is different from those of the heavier analogs of alkali−metal organic complexes; C−Na to C−Cs bonds are acknowledged to be even more ionic than the C−Li bond. It was therefore felt that a certain percentage of covalent character may be associated with the C−Li bond[3]. But recent studies and developments of methodologies for the analysis of wave functions and charge distributions suggest a much higher polarity to the bond. In 1995, Streitwieser, Bachrach and Schleyer[2]suggested: ‘The carbon lithium bond in theory and in chemical properties can be modeled as an essentially ionic bond’. They described a number of examples, which support the ionic behavior of the carbon−lithium bond.

Later, Koizumi and Kikuchi[4] used *ab initio* calculations of NMR spin−spin coupling constants in monomeric methyllithium, *tert*-butyllithium and methyllithium oligomers using self-consistent perturbation theory to probe the nature of C−Li bonding. Their studies suggested that solvation affects the nature of the C−Li bond and reduces the $^1J_{\mathrm{CLi}}$ value significantly. The calculations were also carried out using a truncated basis set (the MIDI-4 basis set for lithium which includes only the 1s function and corresponds to lithium cation), which models a purely ionic C−Li bond. The calculated coupling constants were in excellent agreement with experimental data, suggesting the importance of the ionic character of the C−Li bond in alkyllithiums. The calculated $^1J_{\mathrm{CLi}}$ value of methyllithium, 44.0 Hz, is found to be very close to that calculated for methyllithium with three solvating ligands. This result, which strongly suggests the ionic nature of the C−Li bond in methyllithium, does not change with the addition of ligands. The difference between the $^1J_{\mathrm{CLi}}$ values calculated by two different types of basis set for methyllithium tetramer is much smaller than that in monomeric methyllithium. This trend is in accordance with the observation that the coupling constants in methyllithium tetramer are independent of solvent. Comparing the coupling constants of the ring structures **1a, 1b** and **1c** (Figure 1) with the tetrahedral structure **1d** (staggered and eclipsed form) implies that $^1J_{\mathrm{CLi}}$ depends on the state of aggregation rather than on the degree of aggregation. More clearly, $^1J_{\mathrm{CLi}}$ in methyllithium varies nearly inversely with the number of lithium atoms, which are bonded directly to the carbon atom. The implications are that the ionic nature of the monomeric MeLi increases on solvation and the tetrameric MeLi has more ionic C−Li bonding. In addition, further solvation is not desirable as the bridging nature of tetramer provides the effect of solvation.



20.9 Hz
(1a)

24.1 Hz
(1b)

24.6 Hz
(1c)

Staggered 12.5 Hz and eclipsed 14.0 Hz
(1d)

FIGURE 1. The ring structures of the dimer (**1a**), trimer (**1b**) and tetramer (**1c**) of CH_3Li and a perspective representation of the tetrahedral structure (**1d**) of the latter. The calculated coupling constants are given below each structure. Reprinted with permission from Reference 4. Copyright 1995 American Chemical Society

In 1996, Bickelhaupt and coworkers investigated CH_3Li, $(CH_3Li)_2$ and $(CH_3Li)_4$ using Density Functional Theory (DFT) and conventional *ab initio* Molecular Orbital Theory (MOT)^5. This study highlighted the important role of a small covalent component in the polar C−Li bond, especially in the methyllithium tetramer. It was suggested that the lithium outer 2p orbital serves only as 'superposition functions', helping to describe the carbanion, and does not play any part in covalent interaction. However, there appears to be a small contribution from the inner parts of the Li 2p orbital. Streitwieser and coworkers^6 showed that calculations using a truncated basis set on lithium with only s-type basis functions yield essentially the same result (including the energetic ordering of isomers) as calculated using the full basis sets. They concluded that the bonding is governed by electrostatic interactions. The extended 6-31+G* basis set used in the evaluation of aggregation energies was expected to minimize the basis set superposition error as suggested by Bickelhaupt and coworkers^5. The result showed that the oligomerization energies ($\Delta E_{\text{oligo}} + \Delta\text{ZPE}$) calculated with truncated basis set are up to 20% lower than those obtained using the full 6-31+G* basis. This indicated that the bonding mechanism is more complicated than suggested by the purely electrostatic model.

Charges on lithium calculated using the Voronoi Deformation Density (VDD) decrease from 0.38 via 0.26 to 0.13e along CH_3Li, $(CH_3Li)_2$, $(CH_3Li)_4$ showing that the shift of electron density from lithium to methyl decreases upon oligomerization^5. Similarly, Hirshfeld lithium charges decrease from +0.49 via 0.42 down to +0.30e along the same series of methyl lithium oligomers (Table 1). The fragment molecular orbital analysis shows $(CH_3^\bullet)_n$ and $(Li^\bullet)_n$ fragments to have triplet and quintet electronic structures in $(CH_3Li)_2$ and $(CH_3Li)_4$, respectively. Thus the interacting fragments are two singly occupied molecular orbitals ($SOMO_{\text{low}}$ and $SOMO_{\text{high}}$) in each $(CH_3^\bullet)_n$ and $(Li^\bullet)_n$. The

TABLE 1. The charges of Li in CH_3Li and its oligomers. Reproduced with permission from Ref. 5

Method	CH_3Li	$(CH_3Li)_2$	$(CH_3Li)_4$
Voronoi deformation density (VDD)	0.38	0.26	0.13
Hirshfeld	0.49	0.42	0.30

above trend of decrease in electron density transfer from lithium is in accordance with the increasing population of the $(Li^{\bullet})_n$ fragment orbitals $SOMO_{low}$ and $SOMO_{high}$ from $(CH_3Li)_2$ [$SOMO_{low} = 0.57$ and $SOMO_{high} = 0.63$] to $(CH_3Li)_4$ [$SOMO_{low} = 0.91$ and $SOMO_{high} = 0.85$]. This is indicative of the increasing importance of a covalent component in the carbon–lithium bond. Also, the carbon–lithium bond is much less ionic according to Hirshfeld[5] (50–30%) than according to NPA charges (90%). These factors suggest that the degree of ionicity of a bond obtained on the basis of atomic charges should not be regarded as an absolute quantity, rather it will be more meaningful to consider trends in atomic charges across a series of molecules using the same method. Even though Bickelhaupt[5] emphasized the importance of covalent contributions to the C–Li bonding, the results imply the 'dual nature' of the C–Li bond. It can be concluded that the appearance of a covalent or ionic aspect depends strongly on the physical and chemical context.

From their analysis of the conformational energies of pentadienyl anion and the pentadienyl metal compounds, Pratt and Streitwieser[7] in 2000 pointed out that the stabilization of the planar forms of the organometallic structures results from both conjugation and electrostatic attraction between the negative carbons and the alkali metal cations. To determine the relative magnitude of these effects, the reaction energies were determined for hypothetical reaction, shown in Scheme 1 where M represents any alkali metal.

SCHEME 1

The reaction energies for the formation of pentadienyllithium are found to be much greater than those for pentadienyl sodium, which indicate a greater electrostatic attraction for the shorter Li–C bond. The calculated regional charges for the pentadienyllithiums (HF/6-311+G*) indicate that the most positive charge is concentrated on lithium and the most negative charge is concentrated on the carbon atom coordinated to the lithium. These results imply an ionic nature of the C–Li bond in pentadienyllithium. However, the larger magnitude of electrostatic interaction may be due to the shorter distance of the C–Li bond, and not necessarily to a larger charge separation. In other words, it is possible that the charge on lithium may be less than that on sodium in the corresponding sodium derivative and yet the electrostatic interaction may be larger in the former due to the shorter distance.

Density functional theory calculations on methyllithium, *tert*-butyllithium and phenyllithium oligomers by Kwon, Sevin and McKee support the ionic character of the C–Li bond[8]. Their calculations of carbon lithium Natural Population Analysis (NPA) charges and dipole moments for CH_3Li, *t*-BuLi and Ph-Li oligomers (Table 2) indicate the ionic behavior of the C–Li bond. Comparison of the charges of various oligomers suggests that charges of lithium and carbon atoms are almost independent of the size of oligomers. There are minor variations in the charge of the Li on going from CH_3Li via *t*-BuLi and PhLi, implying that there are changes in the nature of C–Li bonding as a function of the organic group. Thus it is not correct to say that all C–Li bonds are 100% ionic. There are minor variations.

TABLE 2. The charges on Li and, C coordinated to the Li and the dipole moments for a series of MeLi, *t*-BuLi and PhLi oligomers. Reproduced with permission from Ref. 8

	NPA charge[a]		Dipole moment[b]
	Li	C	
MeLi (monomer)	0.83	−1.48	5.51
Me_2Li_2	0.87	−1.53	0
Me_3Li_3	0.84	−1.51	0
Me_4Li_4	0.86	−1.51	0
t-BuLi	0.81	−0.59	6.23
t-Bu_2Li_2	0.87	−0.71	0
t-Bu_3Li_3	0.82	−0.69	0
t-Bu_4Li_4	0.85	−0.74	0
PhLi (monomer)	0.87[c]	−0.64[c]	6.61
Ph_4Li_4	0.85[c]	−0.69[c]	0

[a] At the B3LYP/6-31+G* level where diffuse functions have been omitted from lithium atoms.
[b] At the B3LYP/6-31+G* level.
[c] At the B3LYP/6-31+G* level where diffuse functions have been omitted from lithium atoms and carbon atoms not coordinated to the lithium face.

Ponec and coworkers[9] reconsidered the conventional concept of C−Li bond in CH_3Li and CLi_6. Their calculations were based on two recently proposed methodologies: the Atoms in Molecule (AIM) generalized population analysis and Fermi hole analysis. These results support the ionic nature of C−Li bonding in CH_3Li, but in CLi_6 a different description than the one published earlier[2] is suggested. The bonding description of CLi_6 proposed by Schleyer and coworkers in 1995 involves a C^{4-} ion surrounded by Li_6^{4+} in an octahedral fashion (Figure 2). The two electrons in the lithium cluster are placed in an orbital, which is completely symmetric, being a Li−Li bonding orbital among all lithium atoms, with a small contribution from the carbon 2s orbital. This extra electron pair was considered as a part of the Li$\cdots$Li bonding interactions. According to Ponec

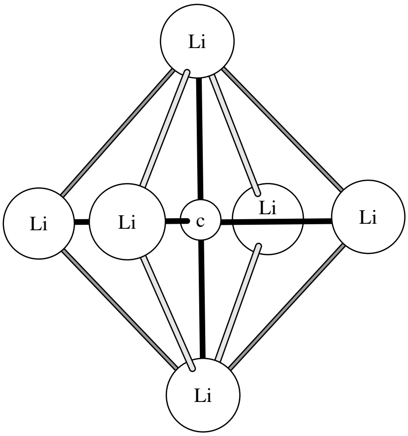


FIGURE 2. Optimized structure of CLi_6 at HF/6-31G*. Reproduced by permission of J. Wiley & Sons from A. M. Sapse and P. v. R. Schleyer (Eds.), *Lithium Chemistry. A Theoretical and Experimental Overview,* J. Wiley & Sons, New York, 1995

and coworkers the AIM analysis suggests that this electron pair is also shared between the carbon and lithiums and the contributions of C and Li are roughly equal to 1.2 and 0.8*e*, respectively. Although the oxidation state of the central carbon is indeed close to the NPA estimate (−IV), the interactions between the central atom and the surrounding cage need not be purely ionic as expected so far. This is supported by the result of generalized population analysis, which detects the presence of 3-center bonding interactions in Li−C−Li fragments as seen from the values of the corresponding indices, such as the C · · · Li cage interactions. The Li · · · Li bond indices drop from 0.167 (Mulliken-like analysis) to 0.020 (AIM generalized value), correlating the conclusions above.

Thus it is evident from all these studies that the nature of the C−Li bond varies from compound to compound; hence any generalization of the nature of bonding is to be taken cautiously. As Schleyer and Streitwieser have discussed in the past, the C−Li bond is essentially ionic; however, the covalent components cannot be neglected[5]. The unusual behavior of the C−Li bond has been a subject of discussion from the initial years of applying theoretical methods, and the debate continues in an interesting manner due to the developments of new theoretical methodologies. In fact, we support the implications of Bickelhaupt that there is a covalent contribution to the C−Li bonding, however small this turns out to be in specific examples[5].

III. STRUCTURE AND ENERGY

Theoretical studies of the structure of organolithium compounds continue to attract much attention for several reasons. Often, it is not possible to obtain detailed structural information from experiments. Experimental realization of a single crystal, which is good enough for X-ray diffraction studies, is not always easy. Even when such detailed information about the structure is available, theoretical studies provide an electronic structural description that helps one proceed further. The theoretical results depend on the level of theory used. This often results in the re-examination of structures studied earlier using lower levels of theory. Many of the structures that were thought to be minima were found to have several imaginary frequencies at more sophisticated levels of theory. Schleyer and coworkers in 1995 discussed a large number of compounds and their optimized structures. We consider here results that have appeared since then. Optimized structures and the factors affecting the stability are discussed below. The last ten years have witnessed a revolution in modeling solvent effects. Several theoretical studies incorporating the effect of solvents are known and we first discuss this aspect of structural studies.

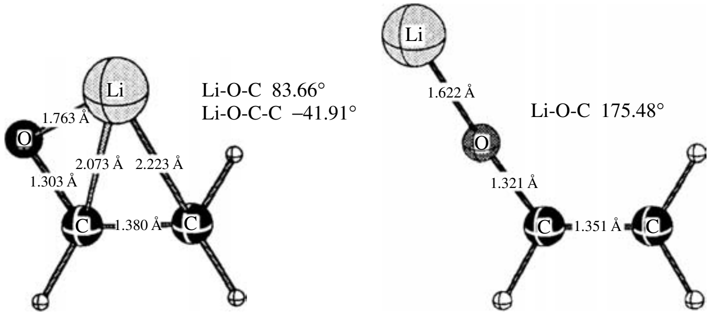
A. Effect of Solvation

The structures of organolithium compounds are affected by solvation. For example, Sorger, Schleyer and Stalke have shown that the solid-state cisoid dimeric structure of 3,3-dimethyl-2-(trimethylsilyl)cyclopropenyllithium-tetramethylenediamine does not persist in solution; it is monomeric in THF solution[10]. In 1996, Weiss and coworkers studied the effect of specific and nonspecific solvations by THF on methyl isobutyrate aggregates[11]. This study shows that the solvent influences the stability of the dimer to a higher extent than that of the tetramer. In total disagreement with earlier experimental results, *ab initio* MO calculations (gas-phase studies) at the MP2/SVD//SCF/SVD, SCF/SVD//SCF/SVD and SCF/TZD//SCF/SVD (split valence basis sets augmented with one d-polarization function for carbon and oxygen, for Li augmented with one p-polarization function and a double-ζ basis set for hydrogen; this is referred to as SVD; the Karlsruhe TZP basis sets for Li, O and C, and for hydrogen the same DZ basis set as for the structure optimization have been used, is referred to as TZD) levels for the energies of dimer and cubic tetramer, suggest that the tetramer is more stable than the dimer. But the results of solvent effects, using the semiempirical MNDO and PM3 methods, predict the dimer to be more stable[11]. Clearly, more careful investigation is required here before definite conclusions can be drawn. The general indication is that the dimers are more strongly affected by solvation than the tetramers.

Since several aspects of the regio- and stereoselectivity of lithium enolates involves the characteristics of their aggregation, the effect of solvation on the structure and aggregation of lithium enolates plays an important role in the mechanistic study. In 1997, Abbotto, Streitwieser and Schleyer investigated theoretically by using *ab initio* and semiempirical MO methods the effect of ether solvent on the aggregation of lithium enolates[12]. This study shows that solvation has a critical role in determining the relative energies of the aggregated species. π-Interaction between lithium and the enolate double bond is another factor that helps to determine the relative stabilities of the isomers and the degree of solvation. The cubic tetramer is stable because of the electrostatic stabilization of the aggregation, but the monomeric species is important in the equilibrium owing to its high solvation energies. In contrast, the dimer, and to a greater extent the trimer, is less important. The tendency of lithium cation to reach tetracoordination is shown to be less significant than commonly believed. Jackman and Lange studied the aggregation and reactivity of lithium enolates using ^{6}Li and ^{13}C NMR spectroscopy and suggested that the parent lithium enolate of acetaldehyde exists exclusively as a tetramer in THF solution[13]. Selection of water as a solvent molecule in the study of the solvation effect is less effective due to the property of water to form hydrogen bonds. In their study Abbotto and coworkers abandoned THF as the solvent due to its large size and took dimethyl ether as a realistic coordinating solvent[12].

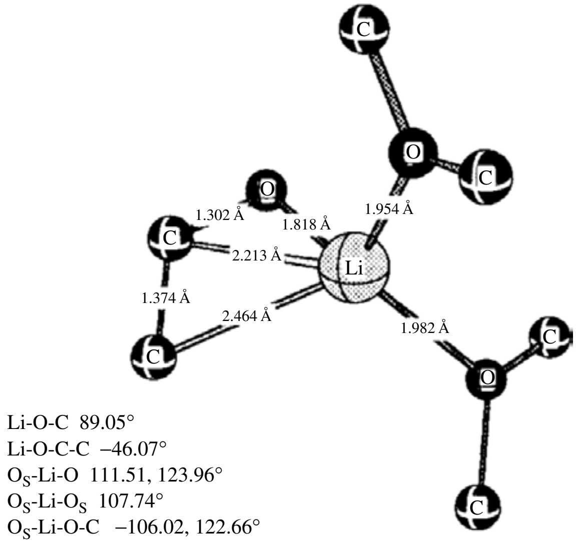
The effect of solvation in $CH_2{=}CHOLi$ was studied in detail. Earlier studies at the B3LYP/6-31+G* level suggested that the lowest energy minima correspond to isolated bridged lithium enolate **2a**, rather than the open-chain structure **2b**; this is attributed to the interaction of the lithium cation with the enolate anion (Figure 3).

The main consequences of the solvation are found to be the increment in bond lengths between the enolate oxygen atom and the lithium in the mono and the disolvated (**3a**) enolates, together with the increment in the Li–Osolvent bond. However, the trend continues up to trisolvated species **3b** (Figure 4), where the Li–O distance is found to be less than that in isolated species. These characteristics of larger Li–dimethyl ether distance (due to the steric hindrance) and the absence of coordination to the double bonds suggest an ionic interaction of Li with enolate oxygen.

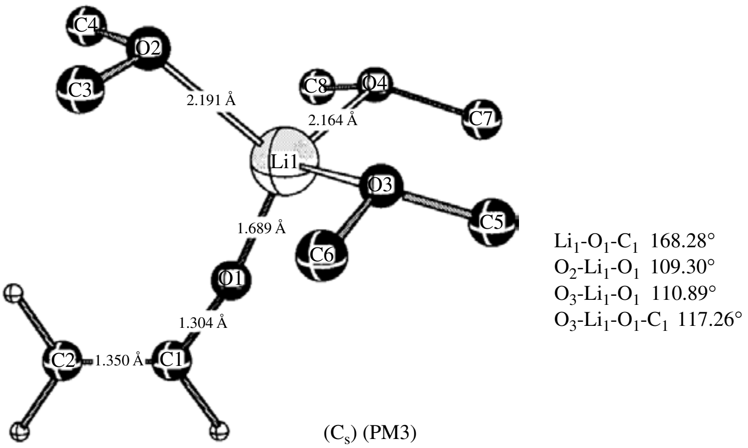


(2a) **(2b)**

FIGURE 3. Optimized structures of monomer $CH_2{=}CHOLi$ as obtained from B3LYP/6-31+G* calculations. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society



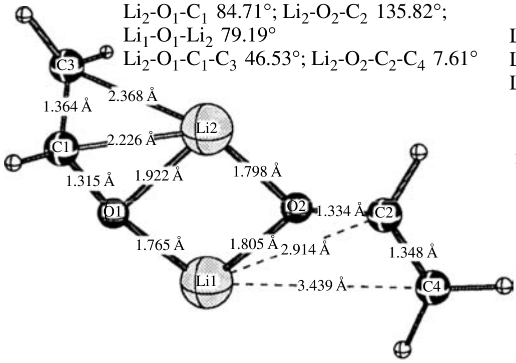
(B3LYP)
(6–31 + G*)
(3a)



(C_s) (PM3)
(6–31 + G*)
(3b)

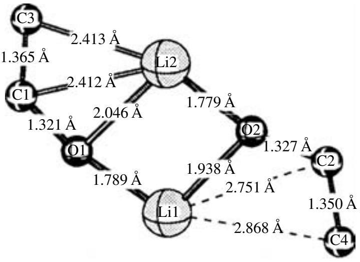
FIGURE 4. Optimized structures of $CH_2{=}CHOLi(Me_2O)_2$ (**3a**) as obtained from B3LYP/6-31+G* calculations (**3b**) and $CH_2{=}CHOLi(Me_2O)_3$ as obtained from PM3 calculations. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society

The geometries for the dimeric isomers are also optimized at the B3LYP/6-31+G* level. The results were compared with Hartree–Fock and PM3 results. The stable dimers **4a, 4b** and **4c** are found to have C_1 symmetry (Figure 5).



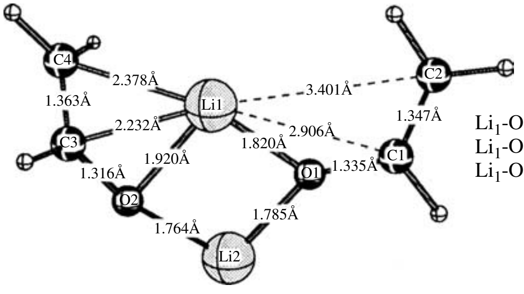
Li_2-O_1-C_1 84.71°; Li_2-O_2-C_2 135.82°;
Li_1-O_1-Li_2 79.19°
Li_2-O_1-C_1-C_3 46.53°; Li_2-O_2-C_2-C_4 7.61°

(C_1) (B3LYP)
(4a)



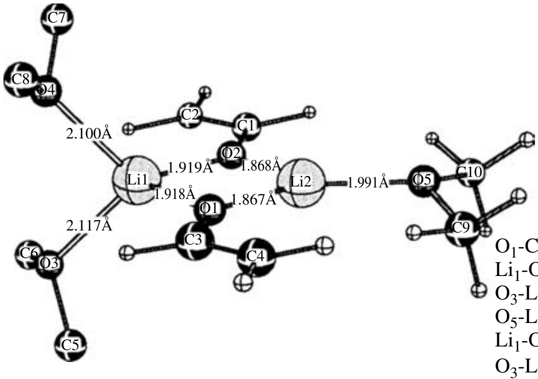
Li_2-O_1-C_1 88.82°; Li_2-O_2-C_2 113.49°;
Li_1-O_1-Li_2 79.21°
Li_2-O_1-C_1-C_3 38.98°; Li_2-O_2-C_2-C_4 −0.88°

(C_1) (PM3)
(4b)



Li_1-O_2-C_3 85.05°; Li_1-O_1-C_1 133.60°;
Li_1-O_2-Li_2 79.14°
Li_1-O_2-C_3-C_4 46.62°; Li_1-O_1-C_1-C_2 4.13°

(C_1) (B3LYP)
(4c)



O_1-C_3 1.32 Å; C_3-C_4 1.35 Å
Li_1-O_1-C_3 130.97°; O_2-Li_1-O_1 85.94°
O_3-Li_1-O_1 118.20°; O_4-Li_1-O_3 91.07°
O_5-Li_2-O_1 137.72°
Li_1-O_1-C_2-C_4 −176.65°;
O_3-Li_1-O_1-C_3 −52.59°

(C_1) (PM3)
(4d)

FIGURE 5. **4a–4c** are optimized structures of dimers $(CH_2{=}CHOLi)_2$ as obtained from B3LYP/6-31+G* and PM3 calculations. Hydrogen atoms are omitted in PM3. Structure **4d** represents the optimized structure of the complex of the dimer $(CH_2{=}CHOLi)_2$ with three molecules of Me_2O at the PM3 level. Reprinted with permission from Reference 12. Copyright 1997 American Chemical Society

The relatively high stability of the three isomers **4a, 4b** and **4c** is attributed to the stabilizing interaction between lithium cation and enolate double bond. Comparison of the energy of monomer, dimer and trimer systems, with and without π-coordination (as in **2a** vs **2b** in Figure 3) indicated the π-coordination energy to be 0.5–2.6 $\mathrm{kcal\,mol^{-1}}$. It is found that for the trisolvated monomer **3b** (and for other aggregates) π-coordination disappears on solvation (Figure 4). Thus π-coordination is also a decisive factor in determining the most favorable degree of solvation. Abbotto and coworkers concluded that if the negative entropic contribution relative to the third solvation process of monomeric $CH_2{=}CHOLi$ is assumed to be about 5–10 eu, the small negative enthalpy suggests that this step has a positive ΔG at room temperature. Thus it is clear that tetracoordination of the lithium center is not necessarily a thermodynamically favored process; less solvated species with coordinated lithium may well be more stable. If we consider the solvation enthalpies and entropies, the most stable solvated species are the disolvated monomer **4a**, the trisolvated dimer **4d**, the trisolvated trimer **5a** and the tetrasolvated tetramer **5b** (Figures 5–6). The association energies among these solvated species are monomer/dimer -14.9, monomer/trimer -11.6 and monomer/tetramer -17.2 $\mathrm{kcal\,mol^{-1}}$ (per mol of monomeric unit). Comparison of these values with the corresponding energies without solvation of -26.0, -33.5 and -35.3 $\mathrm{kcal\,mol^{-1}}$ (which are increasing in the order monomer/dimer < monomer/trimer < monomer/tetramer) suggests a different order with the monomer/dimer equilibrium being the least favored.

The calculations of the natural charge populations of selected B3LYP/6-31+G* optimized structures, using the two different basis sets 6-31+G* and 6-311+G**, reveal the increase of negative charge on the oxygen, and a decrease on the carbons on aggregation (Table 3). The results are rationalized as follows. Compared to the monomer, each oxygen of the dimer is close to two positively charged lithium centers and, as a consequence of its higher effective electronegativity, it removes more charge from the double bond. The increase in the charge on oxygen is about the same as the decrease in C_β charge. In the dimer in which the π-coordination is absent, the lithium atom carries more positive charge. Hence the oxygen of the bridged unit is effectively less electronegative and less charge is withdrawn from the α-carbon. This fact suggests that the π-coordination between the enolate double bond and the lithium cation increases the negative charge by about 0.1 electron at the β-position. The lack of significant difference observed between the carbon of the bridged unit in **4a** in Figure 5 and the corresponding position of the C_{2h} isomer (Figure 7) suggests that the π-delocalization from oxygen to the double bond is not important and that the polarization mechanism controls charge redistribution in lithium enolates. This is also reflected in the identical distances of O–C and C–C bonds[12] in the unbridged enolate unit of C_1 isomer (Figure 5) and in the C_{2h} isomer **6** (Figure 7).

The decrease in the negative charge on C_β on going from monomer to higher aggregates implies the opposite behavior in the solvated monomers. The reverse behavior is due to the bonding of lithium to more oxygens on solvation. Thus the solvation limits its effect on charge redistribution primarily to the lithium cation, and the populations on the enolate moiety are relatively unaffected by solvent contribution.

B. Stability due to Sulfur

The high nucleophilicity of heterosubstituted allyllithium compounds makes them attractive reagents in synthetic organic chemistry. Structural studies of these compounds give a fundamental understanding about the control of the regioselectivity. Often, these studies are difficult due to the tendency of the compounds to form complex fluxional aggregates in solution. Piffl and coworkers have studied the dependency of the oxidation state of sulfur on the structure and electronic properties of the heterosubstituted