

Ab initio theoretical study of 3-aminopyrrolidines lithium amides as chiral ligands for butyllithium

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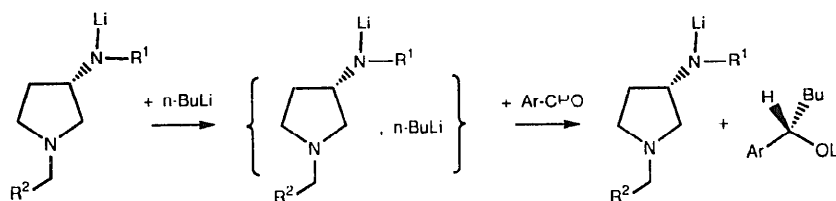
Abstract

DFT computations on 3-*N*-methylamino-*N*-methylpyrrolidine lithium amide and its complex with methyl lithium are reported. The results obtained fully support the norbornyl-like folding adopted by the pyrrolidine ring that has been inferred from experimental NMR data. The ⁶Li and ¹³C theoretical nuclear magnetic shielding constants are in reasonable agreement with the corresponding measured chemical shifts for parent compounds. The comparison between experimental and theoretical results confirms that, for the 3-aminopyrrolidines experimentally studied, there is, in solution, a delicate balance between steric repulsions and aggregation forces. On the other hand, the model systems considered in this preliminary study are able to account for the energy scale of most of the different possible intermolecular interactions but not for the driving forces at work in the aldehyde–lithium amide condensation reaction. © 1997 Elsevier Science S.A.

Keywords: DFT; Lithium amides conformation; Lithium amide–alkyllithium complexes

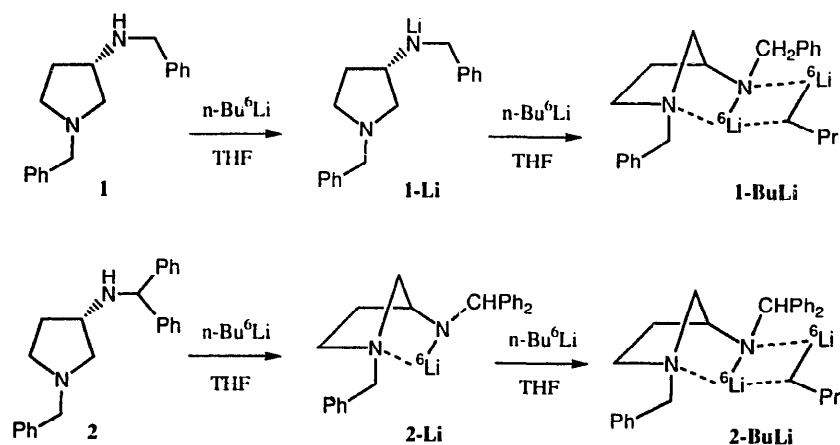
1. Introduction

Chiral lithium amide (CLA) have found many applications as chiral auxiliaries in enantioselective organic synthesis [1–3]. However, only a very few applications of CLA–alkyllithium systems have been reported to date [4,5]. Recent experimental results [5] have shown that several chiral 3-alkylaminopyrrolidines (3-AP) lithium amides are able to provide e.e. (enantiomeric excess) up to 77% in the asymmetric condensation of butyllithium on aromatic aldehydes



A low-temperature multi-nuclei high-field NMR study has been undertaken on two 3-AP lithium amides (**1-Li** and **2-Li**) in THF [6]. The deprotonation of the amines **1** and **2** by *n*-Bu⁶Li yielded ⁶Li amides (Scheme 1) on which homonuclear (¹H–¹H and ⁶Li–⁶Li) and heteronuclear (¹H–¹³C and ¹H–⁶Li) correlation experiments (COSY, EXSY,

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Scheme 1.

HOESY) have provided indications on the three dimensional arrangements of these species. The results seem to indicate that **2-Li** adopts a folded (norbornyl-like) structure, while that of **1-Li** could not be determined. The same set of experiments achieved on mixtures of **1-Li** or **2-Li** with $n\text{-Bu}^6\text{Li}$, in experimental conditions comparable to those used in the BuLi-aromatic aldehydes asymmetric condensation, led to the conclusion that a stable complex between the CLA and butyllithium is formed prior to reaction with the aldehyde. The structure of the two complexes **1-BuLi** and **2-BuLi** appeared to share a folded topology close to that of **2-Li** (Scheme 1). The formation of such mixed aggregates had previously been proposed [7] but has only recently been observed in one case from ^6Li NMR experiments on the complex between the N-(1-methoxy-2-phenylethyl)-2-phenylethylamine lithium amide and butyllithium [8–10]. By contrast, the structure of organolithium compounds in solution has been the object of a considerable attention on both experimental and theoretical point of view. Ab initio calculations dealing with the reaction between methyl lithium and formaldehyde have shown that MeLi dimer is the reactive entity toward the aldehyde substrate [11,12]. In the case considered here, the condensation should take place between a butyllithium, that may or may not be complexed to the CLA, and the aldehyde. Many experimental and theoretical investigations have also shown previously that the solvent (and especially THF) steps in the aggregation phenomenon of lithiated species [8,13–18]. Semi-empirical and ab initio computations concerning methyl lithium [14] indicate that amines yield larger solvation enthalpies than corresponding ethers. By contrast, MNDO computations on model lithium amides have led to the opposite conclusion and shown that steric factors have a major influence on the aggregation state [15,16].

The theoretical study presented here has a two-fold purpose.

(i) To investigate the thermodynamic aspect of the lithium amide–butyllithium interactions at the origin of such complexes, the existence of which relies on relatively restricted spectroscopical grounds. Given these data, the comparison of the theoretical and experimental conformations will provide information on the influence of the substituents and/or the environment on the conformational parameters. The comparison between calculated and (available) experimental chemical shifts will allow an evaluation of the quality of the agreement between experiment and theoretical results.

(ii) Getting some information on the BuLi–aldehyde condensation mechanism which is a particularly challenging problem. The organometallic entity is indeed expected to interact with the aldehyde through a metal–carbonyl docking [19,20], leading to a possible pre-transition state complex which remains out of reach of available experimental methods [21]. The study of the interaction energies of a model lithium amide with models of the various entities present during the reaction, will possibly give some insights into the driving forces at work during the reaction and thus indications on the factors governing the stereochemical efficiency of such chiral auxiliaries. Previous theoretical studies have indeed shown that the enantioselectivity of a reaction can, in general, be related either to the interaction energy between the reactants [22] or to the conformation of the chiral substrate [23] even if, in some cases, both of these phenomena have to be taken into account [24].

2. Computational details

The calculations were carried out using Gaussian 94 [25] with the 6-31G** [26] basis, and the Becke3P86 hybrid density functional [27,28]. We had to resort to DFT instead of MP2 to take into account electron correlation because

of the size of the largest of the systems to be considered. Since nowadays literature provides with numerous studies [29–34] showing that, for closed-shell systems, the two computational procedures lead to similar results, we did not think necessary to run any MP2 calculations to verify that this agreement holds in the present cases. However, and because some the interaction energy values obtained were numerically very close, a small number of computations on the entities concerned were repeated using the B3LYP functional which is increasingly taken as standard [35–41]. These runs were carried out to verify the result's qualitative features as a function of the choice of the functional.

For all the molecules/complexes considered the geometries were fully optimized and the nuclear magnetic shielding constants reported were calculated, for the optimized structures, using Gauge Invariant Atomic Orbitals [42] and the DFT orbitals. For 3-methylamino-*N*-methylpyrrolidine (3-MAMP), the NMR shielding constants computations were repeated using the B3LYP functional to delineate, for this quantity, the sensitivity of the computed values to the functional retained. The theoretical chemical shifts values refer to methane for ^{13}C and ^1H and to $\text{Li}^+(\text{H}_2\text{O})_6$ for ^6Li .

In the first part of this study, the model CLA chosen for the conformational study is 3-MAMP, while methyl lithium is taken as a shorter model of butyllithium in the case of the complex. In the second part of this ab initio preliminary study, the interactions considered are those taking place between lithium dimethylamide, the simplest lithium amide model already retained by Romesburg and Collum [16] with dimethylether, trimethylamine and formaldehyde, taken respectively as models for the THF, the pyrrolidine nitrogen and the electrophilic reagent. The dimerization of methyl lithium and lithium dimethylamide as well as the interaction of this latter with methyl lithium are also considered for comparison purposes.

3. Results and discussion

We see from Fig. 1 that the optimized structure of the 3-MAMP lithium amide exhibits a norbornyl-like structure in fine agreement with that inferred for the 3-diphenylmethylamino-*N*-benzylpyrrolidine lithium amide **2-Li** [6]. The lithium is located at a bridging position between the two nitrogens, the longer Li–N distance corresponding to the interaction with the pyrrolidine nitrogen. This result tends to show that such a ring puckering, observed only for **2-Li**, is the intrinsically most stable, energy-wise, conformation of isolated 3-AP lithium amides. Analogous intramolecular coordination by either a nitrogen [8] or oxygen [9,10] atom of the metal of lithium amides has been recently established from multinuclear NMR studies. However, this additional coordination does not imply, for these compounds, a conformational strain such as in our case. In addition, the experimental NMR data tend to suggest that such a bridged conformation is not obtained for **1-Li** in THF [6]. This could be due either to a rapid fluctuation between several puckerings of the pyrrolidine ring or to intermolecular aggregation phenomena. The influence of steric hindrance can be supposed to be at the origin of this difference of structure observed for **1-Li** and **2-Li** in solution.

Our calculations shows that two quasi-isoenergetic conformations (shown on Fig. 2a,b) can be obtained upon formation of the complex between 3-MAMP lithium amide and methyl lithium. In both forms A and B, the norbornyl-like conformation of the 3-MAMP lithium amide undergoes only minor modifications. This result appears in fine agreement with experimental NMR data which show that, in the **1-BuLi** and **2-BuLi** complexes, the pyrrolidine ring of the 3-benzyl and 3-diphenylmethylamino lithium amides both adopts a norbornyl-like structure [6]. The Li–N distances of the lithium amide entity are, as for other lithium amides dimers previously studied, [43,44] increased upon formation of the complex and the shortest Li–N distance is found between the amide nitrogen and MeLi lithium atom (Fig. 2). The Li–C distances are somewhat larger than the Li–N ones. It is worth noticing that the two lithium atoms, the methyl carbon and the amide nitrogen adopt an almost planar arrangement and that the methyl lithium

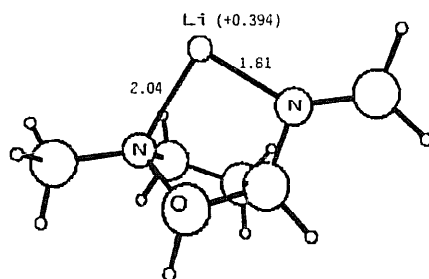


Fig. 1. Optimized structures of 3-*N*-methylamino-*N*-methylpyrrolidine (3-MAMP) lithium amide. Distances are in Å.

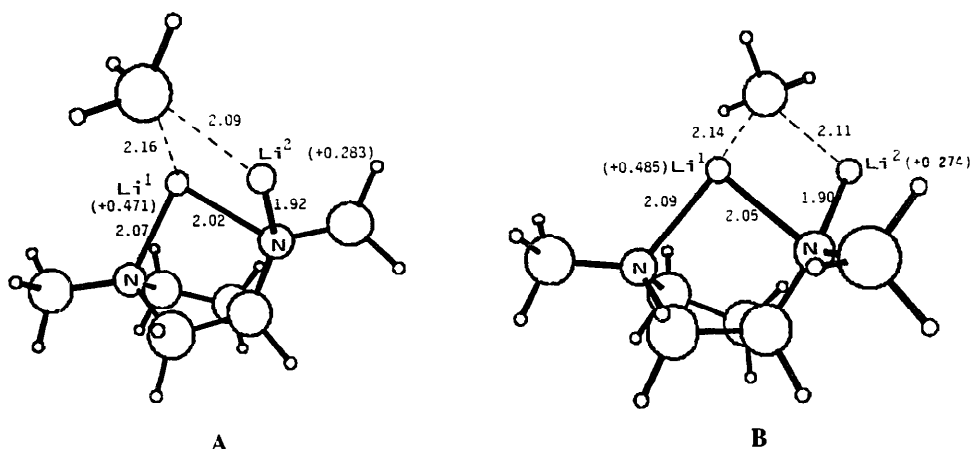


Fig. 2. Optimized structures of the A (left) and B (right) conformations of the complex formed between 3-MAMP lithium amide and methyllithium. Distances are in Å.

carbon atom appears 'hypervalent', as indicated by the small values of the optimized H–C–H valence angles ($102\text{--}104^\circ$) and the unusual range of values for Li–C–H ($80\text{--}140^\circ$). The major difference between the two conformations of the complex concerns the torsion angle about the amide N-methyl group and thus, the location of the methyllithium with respect to the C_2 carbon (Fig. 2). The comparison of Figs. 1 and 2 clearly shows that the formation of the complex induces a pseudo-chirality on the nitrogen atom and that conformers A and B are pseudo-diastereoisomers. Energywise, the interaction between 3-MAMP and methyllithium is calculated to be 49.1 and 48.9 kcal/mol for conformations A and B, respectively, suggesting a slight preference for A. Our results also indicate that, in the complex, the positive charge of the amide lithium (viz. the one exhibiting two short Li–N distances) is significantly larger than that of the MeLi lithium (0.471 vs. 0.283 and 0.485 vs. 0.274 e in complexes A and B, respectively), suggesting that the former lithium could be more electrophile than the latter. Concerning the metal charges, we thus can add that the complex formation increases the charge of the amide lithium while decreasing that of the other one.

Comparing the calculated NMR data to the experimental ones can also come in support to one of the theoretical structures. The calculated values of the nuclear magnetic shielding constants for conformer A give a significantly better fit with experimental data than those concerning conformer B.¹ This result, in addition to the experimental NOESY data [6] and to the above energetical values, tend to exclude conformer B in the cases considered here. Therefore, only conformer A will be discussed in the following.

We have first considered the case of the ^{13}C NMR. Comparison of the measured and calculated shifts reported in Table 1 shows that there is an overall qualitative agreement between experimental and theoretical data except for C_6 and C_7 (Scheme 2) of which substituents are not taken into account in the computations. For the amide as well as for both forms A and B of the complex, theory and experiment give, going upfield:

$$C_2 < C_3 < C_5 < C_4$$

The same relative order of shielding is obtained from the B3LYP computations on the A form of the complex.² We see also from Table 1 that the calculated values of the chemical shift variations due to the complex formation is in reasonable agreement with experiment for C_2 and C_3 but not correctly given for C_4 and C_5 . This disagreement can be attributed either to an unsatisfactory theoretical description of the system or to some puckering fluctuations of the pyrrolidine ring. If such an equilibrium takes place, the NMR data correspond to average chemical shifts while the theoretical values deal only with the more stable one. One should keep in mind that the strong conformational dependence of carbon shieldings in five-membered rings has been shown on experimental [45] and theoretical [46] grounds. Since the C_4 and C_5 are the carbons of the ring the least involved in the interaction with lithium, the $C_4\text{--}C_5$ 'region' is probably the floppiest part of the pyrrolidine ring.

The values concerning the protons shifts, reported in Table 2, show that neither the order nor the chemical shifts variations (with a couple of exceptions) due to the complex formation are correctly given by the theoretical results

¹ Data available upon request.

² $\delta(C_2) = 74.40$, $\delta(C_3) = 73.11$, $\delta(C_4) = 36.98$, $\delta(C_5) = 60.56$, $\delta(C_6) = 46.84$, $\delta(C_7) = 47.86$ ppm.

Table 1
 ^{13}C measured and calculated chemical shifts (δ , ppm)

Carbon	Experimental ^a			Theoretical		
	Amide	Complex	$\Delta\delta$	Amide	Complex	$\Delta\delta$
C ₂	68.3	65.8	2.5	73.21	70.34	2.77
C ₃	61.5	60.5	1.0	71.52	69.82	1.70
C ₄	30.5–31.0	31.1	$-0.6 \approx 0.1$	35.14	31.60	3.54
C ₅	53.5	53.3	0.2	59.47	57.98	1.49
C ₆ ^b	63.3	62.4	0.9	46.45	45.13	1.32
C ₇ ^b	74.4	71.6	2.8	47.05	42.88	4.17

^aTaken from Ref. [6].

^bCarbons C₆ and C₇ in the theoretical model and in the experimental results are different.

Table 2
 ^1H measured and calculated chemical shifts (δ , ppm). The experimental assignment for the gem-protons is tentative

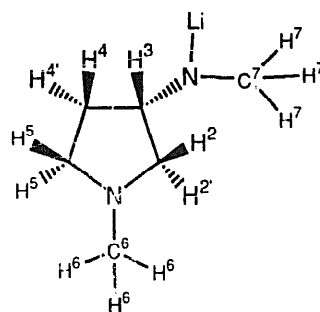
Proton	Experimental ^a			Theoretical		
	Amide	Complex	$\Delta\delta$	Amide	Complex	$\Delta\delta$
H ₂	2.15	1.99	0.16	2.15	2.07	0.08
H _{2'}	2.91	3.22	-0.31	2.34	2.66	-0.32
H ₃	3.11	3.19	-0.08	3.11	3.32	-0.21
H ₄	1.61	1.60	0.01	1.96	2.10	-0.14
H _{4'}	1.91	1.82	0.09	1.70	1.28	0.42
H ₅	2.77	2.68	0.09	2.86	2.79	0.07
H _{5'}	1.91	1.99	-0.08	1.90	1.87	0.03
H ₆ ^b	3.93	2.79	1.14	2.44	2.30	0.14
H ₆ ^b	3.12	4.23	-1.11	2.37	2.54	-0.17
H ₆ ^b				1.61	1.60	0.01
H ₇ ^b	5.00	4.77	0.23	2.78	2.69	0.09
H ₇ ^b				2.68	2.67	0.01
H ₇ ^b				2.27	2.19	0.08

^aTaken from Ref. [6].

^bProtons H₆ and H₇ in the theoretical model and in the experimental results are different.

from B3P86 as well as from B3LYP computations. This discrepancy, if not entirely due to the inadequacy of the theoretical results, confirms the sensitivity of proton shifts to long range through space effects such as those due to the phenyl conjugated rings and/or the solvent [47].

The ^6Li NMR data, gathered in Table 3, agree on the downfield shift undergone by the Li^1 cation upon complex formation and the magnitude of this effect is relatively well reproduced by the calculation (1.19 ppm calc. vs. 0.65 ppm exp.). The ^6Li chemical shift for the monomeric lithium amide is calculated to be 3 ppm upfield with respect to dimeric methyl lithium. Experimentally, it is indeed found upfield, but by only 0.5 ppm with respect to dimeric butyllithium ^6Li signal [48]. In the complex, theory and experiment [6] also agree on the upfield position of Li^1 with respect to Li^2 , even though the theoretical difference is twice smaller than the measured one (0.16 vs. 0.39 ppm). The theoretical Li^2 cation NMR data compares poorly with the experimental ones since the calculated complexation shift is ≈ 2 ppm upfield while a 0.5 ppm downfield shift is measured. Because of the well-known importance of the



Scheme 2.

Table 3
^aLi measured and calculated chemical shifts (δ , ppm)

	Experimental		Theoretical	
	Li ¹	Li ²	Li ¹	Li ²
Amide (R-Li) ²	1.48 ^a	2.05 ^c	1.05	4.15
Complex	2.13 ^a	2.52 ^a	2.24	2.40

^aTaken from Ref. [6].

^bR = *n*-Bu (exp.) or R = Me (theo.).

^cTaken from Ref. [44].

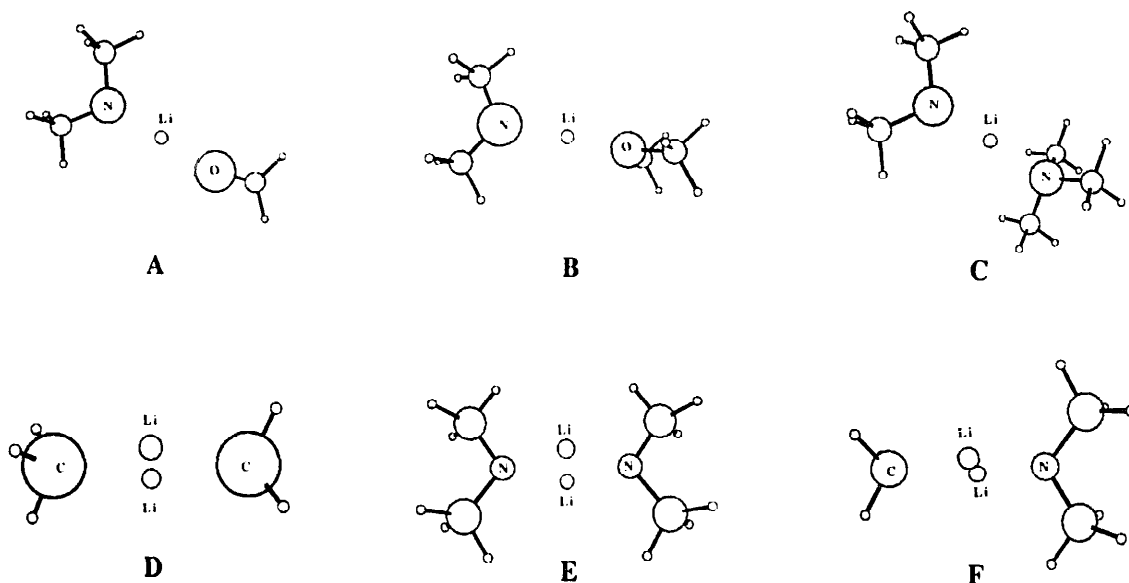


Fig. 3. Optimized structures of lithium dimethylamide (LMA) complexes with formaldehyde (A), dimethylether (B) and trimethylamine (C), of methylolithium dimer (D), LMA dimer (E) and of the LMA-MeLi complex (F).

intermolecular interactions in organic solutions of organolithium compounds, [11–18] [49–51] it seems reasonable to attribute, at least to some extent, a part of the above discrepancies to the fact that the theoretical calculations concern isolated species. We thus thought necessary, in a second step, to investigate the interactions between a model amide and models of its different partners present during the asymmetric condensation reaction studied experimentally [4,5].

For the lithium dimethylamide (LMA) Fig. 3, the values calculated for the different geometrical parameters are close to those obtained by Koizumy et al. [44] at the SCF level with the MIDI-4⁺ plus *p* polarization function on lithium. The largest difference concerns the N–Li distance which is of 1.76 Å from our computations and 1.79 Å from the previous ones [44]. The interaction energies between the lithium dimethylamide and its model ligands are reported in the first three entries of Table 4, altogether with the Li–ligand distances and the lithium net charges. These tabulated values show that when the interaction energy value increases, the Li–ligand distance increases and the

Table 4
 Interaction energies (kcal/mol), equilibrium distances (Å) and lithium net charges (*e*) in complexes of various lithiated species^a

Complex	ΔE	$d(\text{Li}-\text{L}^1)^b$	$d(\text{Li}-\text{L}^2)^c$	$q(\text{Li})$	Fig.
LMA ^d -H ₂ CO	-20.1 (-22.0)	1.801 (1.800)	1.857 (1.847)	0.391 (0.340)	Fig. 3A
LMA ^d -Me ₂ O	-20.7 (-22.4)	1.783 (1.785)	1.912 (1.905)	0.360 (0.314)	Fig. 3B
LMA ^d -Me ₃ N	-21.9 (-22.9)	1.784 (1.784)	2.061 (2.059)	0.349 (0.299)	Fig. 3C
(MeLi) ₂	-22.3 ^e	2.107	2.114	0.365	Fig. 3D
(LMA) ^d	-29.9 ^e	1.946	1.946	0.496	Fig. 3E
LMA ^d -MeLi	-26.2 ^e	1.938	2.118	0.430	Fig. 3F

^aValues in parenthesis correspond to the B3LYP results.

^bL¹ is the left-part of the L¹-L² complex.

^cL² is the right-part of the L¹-L² complex.

^dLMA = lithium dimethylamide.

^eValue per monomer.

lithium charge decreases. The larger interaction energy of the LMA with trimethylamine than with dimethylether is in qualitative agreement with corresponding MNDO results [16] and the observation of a norbornyl like structure for **2-Li**. This finding is also perfectly in line with previous results obtained on Li^+ complexation by H_2O and NH_3 [52,53].

On the other hand, the calculated value of LMA dimerization energy is of -59.7 kcal/mol (that is -29.9 kcal/mol per unit, Table 4) while its interaction energy with trimethyl amine is only of -21.9 kcal/mol. This result suggests that 3-AP lithium amides which do not exhibit large steric hindrance will tend to aggregate. Therefore, the delicate balance [14,53] between steric repulsion and di/oligomerization is most probably at the origin of the different structures observed in solution for **1-Li** and **2-Li**. This behaviour is to be related to the narrow energy range calculated for interaction energies between organolithium and various ligands [13–18,53] (< 2 kcal/mol according to our calculations and < 3.5 kcal/mol from previous studies [13,53]). From the last three entries of Table 4, we calculate the formation of the complex between LMA and MeLi to be favoured by only 0.2 kcal/mol with respect to the two homodimers.³ Such a small energy difference indicates that structural factors will probably be of prime importance for the formation of such complexes between lithium amides and alkyllithium. From the values of Table 4 one would infer that the aldehyde would be poorly reactive toward lithium amides in THF since, according to our computations, the 3-MAMP–ether complex is somewhat more stable (≈ 0.5 kcal/mol) than the 3-MAMP–aldehyde system. This is in contradiction with experimental data demonstrating the possible direct condensation of lithium amides on aldehydes [4,5,55].

These two last results tend to show the limits of LMA as a model to study the interaction which takes place between the lithium amide–alkyllithium complex and the aldehyde at the very first step of the condensation reaction. In order to get a more realistic insight on this crucial recognition process, most probably at the origin of the asymmetric induction, we are currently carrying out calculations on the interactions of the 3-AP–MeLi complex with models of the solvent and of the aldehyde. Results will be reported in due course.

Acknowledgements

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³ The methylolithium dimerization energy calculated here is in excellent agreement with the -22.2 kcal/mol previously reported value [54].

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