Theoretical and structural studies of lithium cyclic amide conformations. Monomers and aggregates

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High level *ab initio* calculations on the conformations of unsolvated and solvated lithium piperidide, **1**, and lithium morpholide, **2**, were carried out. It was found that both monomers exhibit a global minimum for a chair structure with a planar nitrogen, and **2** shows an additional stable pseudo boat conformation. Dimers and amine–lithium amide mixed aggregates were also calculated including discrete solvation; the role of aggregation is clearly shown both by the changes in geometries and in the stabilization energies. Semiempirical calculations carried out on a recently synthesized tetrameric mixed aggregate give a geometry very similar to the structure determined by X-ray diffraction. The present calculations very usefully confirm the likelihood of mixed aggregates of morpholine–lithium morpholide predicted by the carbonylation reactions and not attainable in solid forms.

Introduction

It is known that lithium dialkylamides exhibit large structural varieties and this fact has generated a persistent debate about the relative reactivities of different aggregation states.[1] An enormous body of structural investigations, mostly crystallographic[2,3] and spectroscopic,[4,5] has been accumulated in the last years. These enlightened works, together with kinetic studies,[6] have contributed to the uncovering of the reactivity relationships underlying their role as strong Brønsted bases and useful nucleophiles.[7] We have shown that the different aggregation states[8,9] can be an efficient tool to tune up the reaction toward the production of the desired compound in high yields.[10] The importance of amine–mixed aggregate as a proton source in reactions involving organolithium compounds has been recently reviewed.[11] Concomitantly with the experimental investigations, and partly due to the transient nature of several suggested aggregates, many detailed computational studies of aggregates of lithium dialkylamides[12] have been carried out using *ab initio* and/or semiempirical methods with variable degrees of accuracy,[7,13] according to the size and nature of the systems examined.

Most of all, the above-mentioned experimental and theoretical investigations have been carried out using acyclic lithium amides. Only a few X-ray structures of cyclic lithium alkylamides were determined, among them the lithium piperidide–piperidine mixed tetramer synthesized in our laboratory, which was the first amine–lithium amide mixed tetramer described.[14] Some solution investigations[15] and a few computational studies[16] on cyclic lithium amides have been carried out, probably because of their relatively large size. Nevertheless, cyclic lithium amides have interesting features of important synthetic consequences related to their flexible conformations as well as to their special acidity–basicity properties.[17] Recent mechanistic studies on the carbonylation of acyclic lithium dialkylamides have shown the mediation of cyclic[13c] and open dimers. Our mechanistic studies on the carbonylation of lithium dialkylamides revealed a different behavior of the lithium cyclic amides.[18,10b] The present theoretical investigation intends to address a number of issues related to these experimental results.

Method of calculation

The present work uses mostly the 6-31+G* basis set including diffuse and polarization functions, with the GAUSSIAN-94 system package.[19] Stationary points on the potential energy surface were located at the Hartree–Fock level by use of gradient optimization procedures[20] (Berny optimization procedure). Taking into account our previous calculations on closely related structures, it is expected that electron correlation effects and zero-point-energy corrections have only minor effects on the calculated geometries and energies.[12] Nevertheless, to test the relevance of the electron correlation we have recalculated all the structures localized in the potential energy surface using B3LYP/6-31+G*;[21] density functional theory[22] compares well with MP2 results.[23] For the largest structures, PM3[24] and MNDO[25] semiempirical methods were used. The semiempirical calculations were carried out with the MOPAC 6.0 system of programs, using EF, PRECISE and GNORM = 0.01. All *ab initio* and semiempirical structures were calculated without symmetry constraints and the stationary points were characterized as minima or saddle points by frequency analysis.

Results and discussion

Structure of monomers

The different conformers for monomeric lithium piperidide, **1**, and lithium morpholide, **2**, were calculated by *ab initio*, DFT and semiempirical methods; the calculated energies are given in Table 1. Chart 1 shows the schematic representation of both molecules and some likely aggregates.

The correlation effects have a prominent role in the stabilization of these conformers, as can be seen in Table 1, but these effects are not important for their geometrical characteristics. The energies indicate the preference for the chair conformation: **1b** is less stable than **1a** by several kcal mol^{-1} by all the methods

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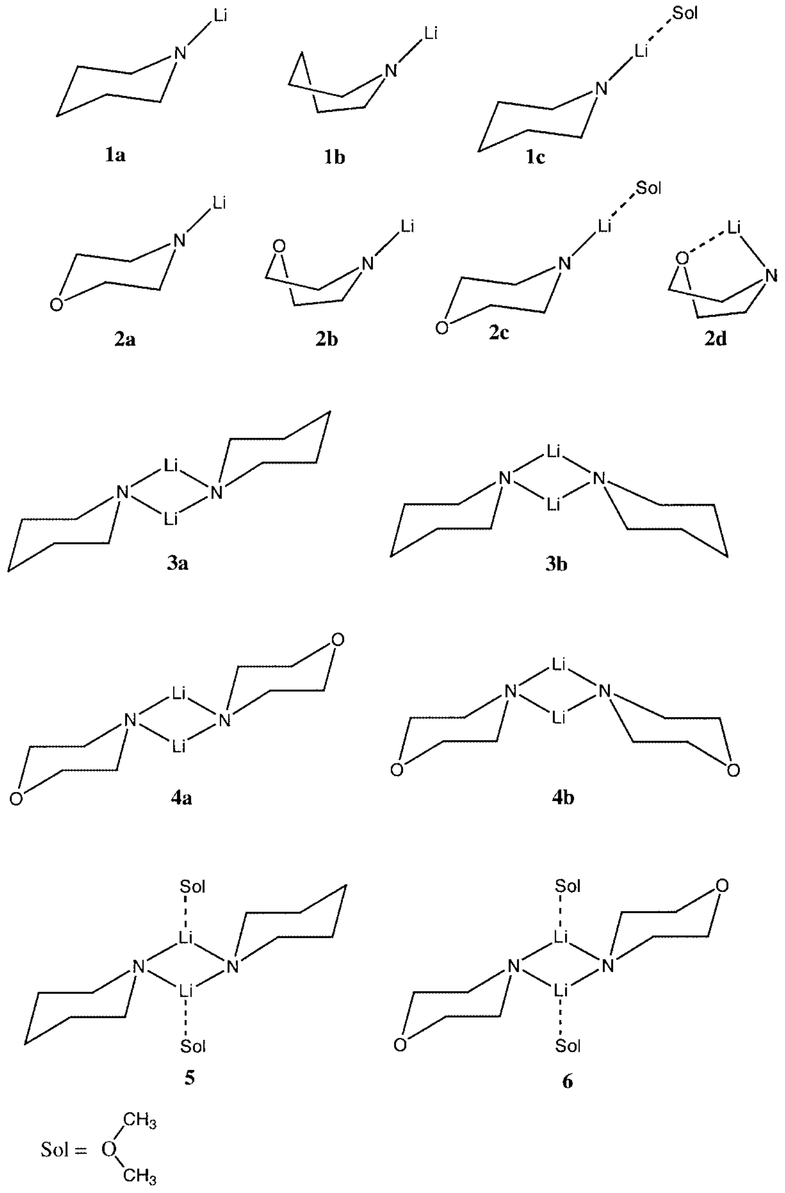


Chart 1

Table 1 Calculated total energies[a] (HF/6-31+G*, B3LYP/6-31+G*) and heats of formation (PM3, MNDO) for the unsolvated cyclic lithium amides

	Total energy/Hartree		Heat of formation/ kcal mol^{-1}	
Molecule	HF/6-31+G*	B3LYP/6-31+G*	PM3	MNDO
1a	−257.048151[a]	−258.834217	5.54	−14.78
1b	−257.036882	−258.805673	9.25	−12.87
2a	−292.862962	−294.728246	−21.53	−43.40
2b	−292.851347	−294.716102	−18.58	−42.13
2d	−292.852482	−294.720300	−11.12	−36.19

[a] Calculated total energy (MP2/6-31+G*) for **1a**: −257.889795 H.

employed. The nitrogen atom of **1** is planar in the monomer, with the H–Cα bond eclipsing the N–Li bond. The strong electropositive character of the lithium atom induces the planarity of N, consistently with previous X-ray diffraction studies of cyclic lithium amides.[14,3]

Table 2 shows selected parameters for all the calculated conformers of **1** and **2**. It can be observed that in the chair and boat conformations of **1** and **2**, the selected bond lengths predicted by HF and DFT are the same. In these cases, the values of the geometrical parameters are very similar by PM3 and MNDO methods, so for the sake of clarity only the MNDO results are reported.

For lithium morpholide, a very interesting new isomer was located on the potential energy surface; it is a pseudo boat structure, **2d**, where the lithium atom is strongly deviated from the planar skeletal framework (see Fig. 1). The marked interaction between the morpholide oxygen and lithium atoms leads to this particular structure, where the lithium is almost equidistant from the N and the O.

As was detailed in previous works, the carbonylation of cyclic lithium amides shows an anomalous behavior.[9,10c] Calculation of the structures of these specific reactants may be able to shed some light on these interesting experimental results.

The carbonylation of acyclic lithium amides [eqn. (1)] is very

$$R^1R^2NLi + CO \longrightarrow R^1R^2NCOH + R^1R^2NCOCOH + R^1R^2NCOCHOHCONR^1R^2 \quad (1)$$

sensitive to the presence of amines in the reaction mixture and they can be used as proton donors to tune up the reaction to the desired target. With the aid of this effect, only one of the three main products can be obtained.

In contrast, carbonylation of **1** and **2** gives only the corresponding formamide irrespective of whether free amine was

Table 2 Selected structural parameters for lithium piperidide, **1**, and lithium morpholide, **2**, in their different conformations

		Bond distances/Å		Atomic charges		
Molecule	Method	N–Li	C_α–N	N	Li	O
1a	HF/6-31+G*	1.76	1.44	−0.04	0.44	
	B3LYP/6-31+G*	1.76	1.45	−0.28	0.38	
	MNDO	1.80	1.44	−0.64	0.53	
1b	HF/6-31+G*	1.76	1.44	−0.27	0.44	
	B3LYP/6-31+G*	1.76	1.44	−0.21	0.15	
	MNDO	1.81	1.44	−0.63	0.53	
2a	HF/6-31+G*	1.76	1.44	−0.37	0.43	−0.31
	B3LYP/6-31+G*	1.76	1.44	−0.14	0.37	−0.46
	MNDO	1.81	1.44	−0.64	0.54	−0.34
2b	HF/6-31+G*	1.76	1.44	−0.32	0.45	−0.32
	B3LYP/6-31+G*	1.76	1.44	−0.07	0.39	−0.46
	MNDO	1.81	1.44	−0.63	0.54	−0.34
2d	HF/6-31+G*	1.87	1.44	−0.43	0.45	−0.36
	B3LYP/6-31+G*	1.87	1.44	−0.24	0.40	−0.51
	MNDO	1.97	1.45	−0.60	0.49	−0.32

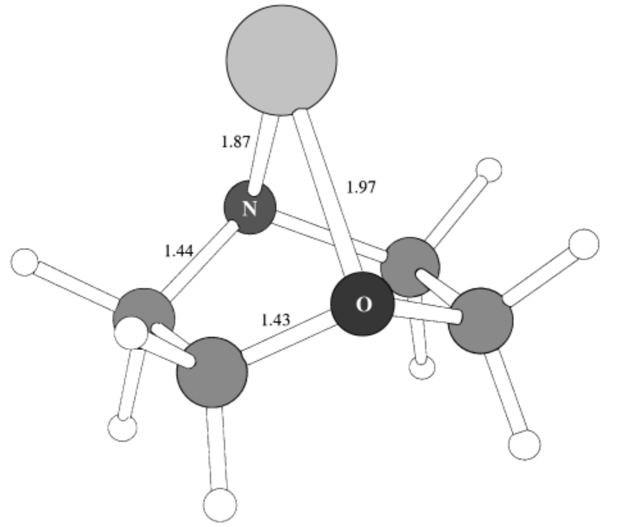


Fig. 1 B3LYP/6-31+G* optimized structure for lithium morpholide, **2d**. Bond distances in Å.

added or not.[9,10c] It was predicted that **1** and **2** could crystallize as mixed aggregates with the amine while prepared, and the further calculations examine different aggregate structures.

Structure of dimers

Organolithium compounds show a strong tendency to form oligomeric aggregates in solution, which influences their reactivity.[26,27] In the solid state[28] and even in the gas phase[29] the propensity of these compounds for association is very well known. Recently, it has been shown that the preferred array for lithium amide oligomers is a ladder structure,[3b,14] rather than a stack[30] or a cyclic one.[31]

Table 3 shows the 6-31+G* and B3LYP/6-31+G* optimized total energies and the semiempirical heats of formation of the unsolvated dimers of **1** and **2** (structures **3** and **4**, respectively, Chart 1). As has been shown before,[12] the correlation energy correction has minor effects for the dimer formation process. *Ab initio* calculations predict N–Li distances which are very close to those found in X-ray studies in similar compounds.[3a,32]

Experimental and theoretical studies have shown that the N–Li bond is essentially ionic.[33,34] As can be expected, the dimers of lithium morpholide and lithium piperidide have a more distributed charge population than the monomers (see Table 4). The *cis* arrangement for the dimers produces a differentiation between the two lithium atoms: while in the *trans* arrangement both lithium atoms have a charge of *ca.* 0.2, in **3b** and in **4b** one lithium atom has a higher density, while the other has a minor charge (0.3 *vs.* 0.1 by HF in **3b**). In **4b** this difference is not so marked, the lithium atoms have a charge of 0.19 and 0.18, respectively. The decrease in the electron charge of the more hindered lithium suggests some multicenter covalent bonding, despite the ionic nature of the N–Li bond.[12]

Table 3 Calculated total energies (HF/6-31+G*, B3LYP/6-31+G*) and heats of formation (PM3, MNDO) for the unsolvated dimer cyclic lithium amides

	Total energy/Hartree		Heat of formation/ kcal mol^{-1}	
Molecule	HF/6-31+G*	B3LYP/6-31+G*	PM3	MNDO
3a	−514.189306	−517.756860	−30.16	−76.35
3b	−514.189307	−517.757317	−30.15	−76.34
4a	−585.816923	−589.545446	−82.55	−131.96
4b	−585.816898	−589.545658	−82.55	−131.96

Solvated monomers and dimers

The degree of solvation is a factor determining the extent of association and geometries around the lithium atom,[35] especially in the cases in which intramolecular solvation is not possible.[36] In order to evaluate the solvation effects on the structure of these lithium amides, calculations with discrete solvation using an explicit molecule of dimethyl ether near the lithium atoms were carried out.

The structure of the dimethyl ether solvated lithium piperidide monomer, **1c**, was minimized; the HF/6-31+G* energy for this compound is −258.00 kcal; since the total energy for the dimethyl ether is −96.68 kcal, the stabilization energy is −20.08 kcal. A deep decrease in the atomic charges of lithium atom and nitrogen is observed, due to the sharing with the oxygen of the ether. Only small differences in the selected geometrical parameters between the solvated and unsolvated molecules were found: the N–Li bond distance is only 0.02 Å longer in the solvated amide.

Semiempirical calculations of solvated forms for dimers were also carried out and the geometrical data are shown in Table 5. Fig. 2 shows the MNDO heats of formation changes (kcal) for dimerization and solvation of lithium piperidide, **1a**, and lithium morpholide, **2a**, (dimethyl ether was found to have a heat of formation of −51.26 kcal mol^{-1} by MNDO). The highly favorable energetic decrease due to the solvation shows a strong preference for the dimer solvated form. Calculations were carried out only with the *trans* conformers, to avoid steric hindrance in the dimers.

The charge redistribution is augmented in the solvated dimers, stressed mainly in the decrease of the positive charge on

Table 4 Selected structural parameters for lithium piperidide and lithium morpholide aggregates

Molecule	Method	Bond distances/Å		Atomic charges			
		N–Li	Li–O_{sv}	N	Li	O	O_{sv}
3a	HF/6-31+G*	1.94		−0.31	0.21		
	B3LYP/6-31+G*	1.94		−0.12	0.17		
	MNDO	2.07		−0.56	0.41		
3b	HF/6-31+G*	1.94		−0.31	0.30/0.13		
	B3LYP/6-31+G*	1.94		−0.11	0.23/0.09		
	MNDO	2.08		−0.56	0.42/0.41		
4a	HF/6-31+G*	1.94		−0.41	0.20	−0.46	
	B3LYP/6-31+G*	1.94		−0.21	0.18	−0.30	
	MNDO	2.08		−0.56	0.42	−0.33	
4b	HF/6-31+G*	1.94		−0.39	0.23/0.18	−0.46	
	B3LYP/6-31+G*	1.94		−0.19	0.19/0.14	−0.30	
	MNDO	2.09		−0.56	0.43/0.42	−0.33	
5	MNDO	2.11	2.17	−0.54	0.28		−0.30
	PM3	2.05	1.94	−0.08	−0.12		−0.14
6	MNDO	2.12	2.16	−0.54	0.28	−0.34	−0.30
	PM3	2.05	1.94	−0.10	−0.09	−0.27	−0.14

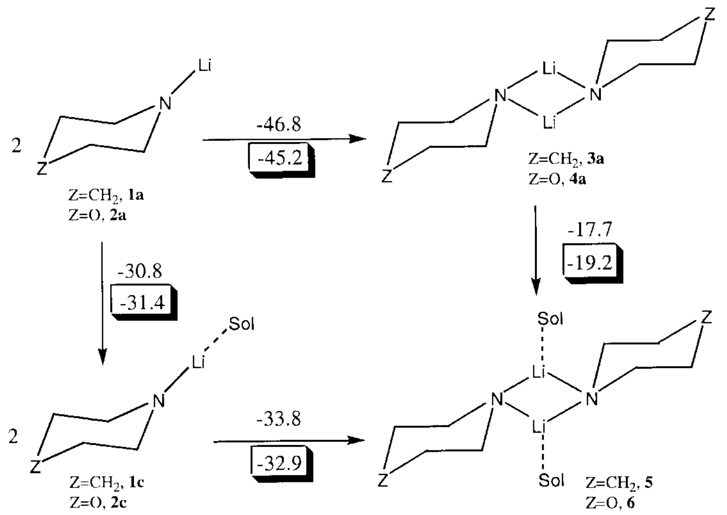


Fig. 2 MNDO energy changes (kcal) for dimerization and solvation of lithium piperidide, **1**. Values in darkened squares are the energy changes for lithium morpholide, **2**.

the lithium atoms. Lengthening of the Li–N bond and a very close interaction with the ether oxygen were found; the rest of the molecule array did not show appreciable variations.

Mixed aggregates

The structure of the first amine–lithium amide mixed aggregate has been recently reported.[14] The 1 : 1 mixed aggregate between lithium piperidide and piperidine has been shown to be a tetramer. This crystal structure agrees completely with research on the carbonylations of lithium amides in solution,[9,10] in which the formation of amine–lithium amides mixed aggregates has been predicted.[10c]

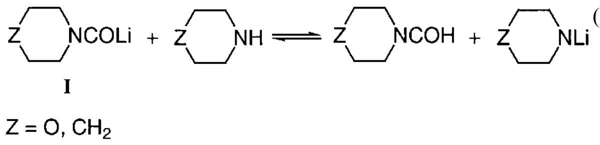
Calculations show the very likely existence of the mixed dimers **9** and **10a** and predict the spontaneous formation of such aggregates when the lithium amides are prepared.

Attempts to crystallize a mixed aggegate morpholine–lithium morpholide were unsuccessful. Therefore, calculations on the structures of mixed dimers and tetramers were carried out by semiempirical methods. The heats of formation and selected structural parameters are given in Table 5. Chart 2 shows the structures of these aggregates.

The formation of dimers **7** and **8** is energetically comparable: −18.1 and −16.1 kcal mol^{-1} for lithium piperidide and lithium morpholide respectively, and the formation of mixed dimers **9** and **10a** is also very close in energy: −20.4 and −20.0 kcal mol^{-1} respectively, showing an extra stabilization. Thus, the existence of a mixed aggregate as **10a** is very likely, and calculations predict the inevitable formation of such lithiated species.[9]

The structures of **9** and **10a** show the existence of a lithium bond between both nitrogens in the molecule. It is known[37] that in an aggregate of two molecules with only one Li atom, a symmetric cyclic arrangement is not possible and in such cases the Li tends to locate directly along the line connecting the donor and acceptor atoms. This arrangement is similar to that found for **7** and **8** (see **8** in Fig. 3), in which the angle NLiN is very close to 180°. The alternative structure, a cyclic geometry containing both a bent H and Li bond calculated for related compounds,[38] was not found in the potential surface for either dimer.

The carbonylation of acyclic lithium dialkylamides usually renders three main products: formamides, glyoxylamides and tartronamide; but the fact that the cyclic lithium amides form mixed aggregates has significant consequences, affording only the alkylformamides. If a molecule of the amine co-crystallizes with the lithium amide, it can react with the highly reactive carbamoyl lithium, **I**, first formed, giving the corresponding formamide hence avoiding further reactions of **I** [eqn. (2)].



(2)

Table 5 MNDO Heats of formation and selected structural parameters for mixed aggregates between cyclic lithium amides and their corresponding amines

Molecule	Heat of formation/ kcal mol^{-1}	Bond distances/Å		Atomic charges		
		Li–N	Li–NH[a]	Li	N	NH[a]
7	−51.54	1.84	2.17	0.32	−0.62	−0.26
8	−104.87	1.85	2.17	0.33	−0.61	−0.26
9	−133.94	2.12	2.25	0.25	−0.54	−0.24
10a	−242.82	2.15	2.26	0.27	−0.54	−0.24
10b	−237.96	2.14	2.19	0.29	−0.54	−0.28

[a] NH = amine nitrogen.

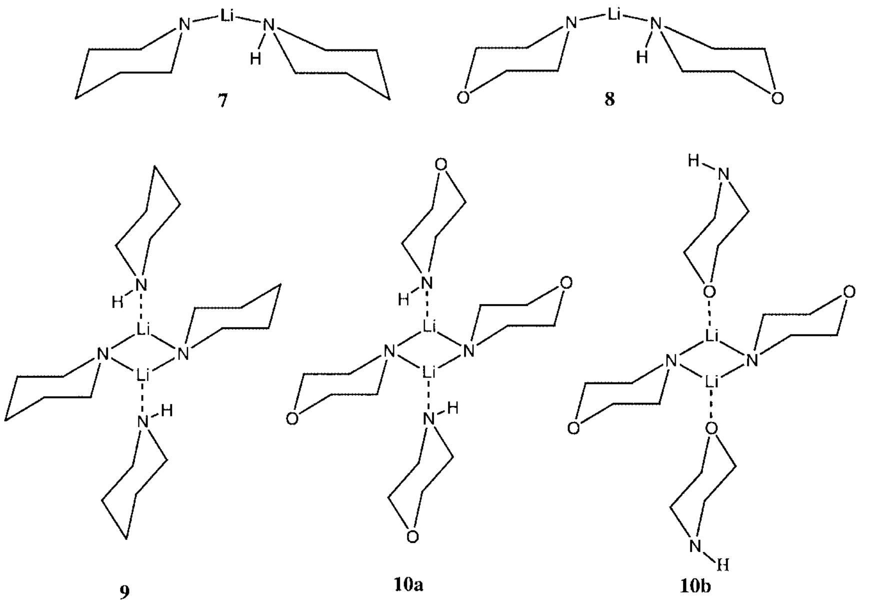


Chart 2

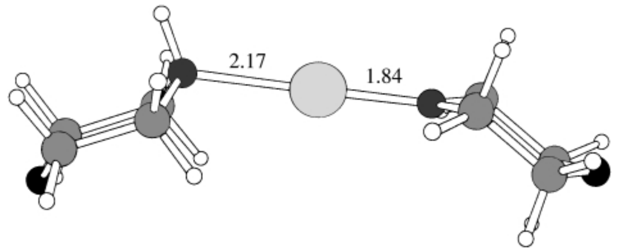


Fig. 3 MNDO optimized structure for lithium morpholide–morpholine mixed aggregate, **8**. Bond distances in Å.

Taking into account its previously determined X-ray structure,[14] the mixed aggregate [Li piperidide]$_4$[piperidine]$_4$, **11**, was also optimized by PM3 methods, finding that the geometrical values of this molecule are almost coincident with the experimental data (see Fig. 4). It has a ladder structure in which the internal eight-membered ring is not planar. The oligomer is also not symmetrical: the tetracoordination reached by the outer lithiums is not favorable for the inner ones due to the higher crowding that exists around these central lithium atoms. Furthermore, the calculated Li–N length in **9** is nicely close to the Li–N length given by X-ray studies on **11**, which gives confidence to the whole calculated results. Cyclic aggregates for [Li morpholide]$_2$[morpholine]$_2$ have two likely arrangements: coordination through nitrogen, **10a**, or, alternatively, coordination through the oxygen, **10b**. As shown in Table 5, the second arrangement, even though very favorable, is somewhat higher in energy than the former, therefore the preferred structure for **10** is **10a**, closely related to that observed in **11**.

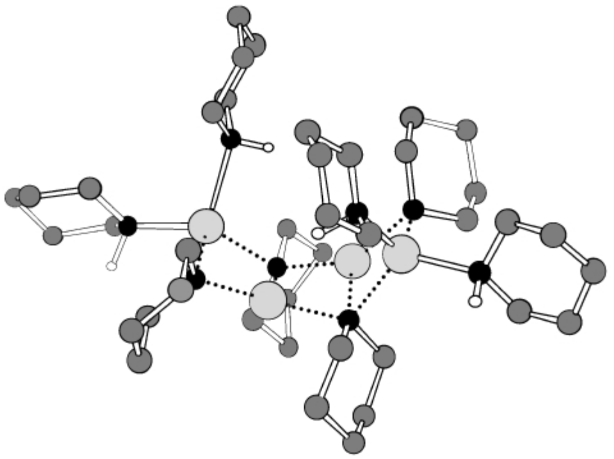


Fig. 4 PM3 optimized structure for [Li piperidide]$_4$[piperidine]$_4$.

The high degree of approximation of both semiempirical methods to the *ab initio* and even the X-ray structures gives high confidence to this sort of calculation.

Conclusions

Besides the preferentially almost chair structure of lithium piperidide, **1**, and lithium morpholide, **2**, exhibiting a planar nitrogen, **2** shows a very special additional conformation in which both heteroatoms are bonded to the lithium. The strong stabilization due to the dimerization and solvation is well predicted even by the semiempirical methods. The calculated structures were coincident with the experimental data when available, which shows that geometries given by the semiempirical methods are highly reliable for this type of reactant when the size of the molecule precludes *ab initio* calculations.

The possible existence of amine–lithium amide mixed aggregates was also investigated. The energetic results show the high probability of tetramer formation, and the geometrical parameters obtained by semiempirical methods for [Li piperidide]$_4$[piperidine]$_4$ are almost in perfect accordance with X-ray measurements. Calculations predict the likely structure for the mixed aggregate [Li morpholide][morpholine] not attainable by experiments, and afford clues for the "anomalous" carbonylations of the lithium cyclic amides.

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