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Theoretical Studies of Chemical Interactions. Ab Initio Calculations on Lithium Dialkylamides and Their Carbonylation Reactions

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Abstract: Lithium dimethylamide (monomer and dimer) and several carbonyl complexes proposed as intermediates in its CO insertion reaction have been investigated by means of ab initio calculations (6-31+G//6-31G and MP2/6-31+G*//6-31G). The calculated values of the main geometrical parameters of the dimer are very close to those from solid-state determinations with stable lithium dialkylamides. The dimerization energy is predicted to be –60.7 and –59.9 kcal/mol at 6-31+G//6-31G and MP2/6-31+G*//6-31G levels, respectively. Calculations show a η^2-coordinated lithium in the first intermediate derived from lithium dimethylamide monomers and CO and a rather long C–O bond (1.30 Å). This indicates a significant alkoxycarbene character, rather than the classical carbamoyl structure. A second intermediate arising from a second CO insertion exhibits a planar geometry with relatively short O–Li bonds and the lithium atom coordinated to both oxygens. The calculations predict the double carbonylation to be a thermodynamically favorable process (–37.6 and 27.7 kcal/mol at 6-31+G and MP2/6-31+G* levels, respectively), in contrast to previous reports but in agreement with experimental results. A third intermediate, formally produced by the coupling of the two just described, shows two η^2-coordinated lithiums and a planar arrangement of the main heavy atoms: the calculated high stability (–85.8 and –91.2 kcal/mol at 6-31+G//6-31G and MP2/6-31+G*//6-31G levels, respectively), explains the high yields of substituted hydroxymalonamides obtained under special reaction conditions. The properties of the tetramethylurea dianion proposed as the precursor for dimethylformamides were also calculated: the high electron density (–1.113) found for the central carbon atom prodicts the facility of this intermediate for producing tetramethylureas.

Introduction

The last decade has seen the rapid development of transition-metal catalysts for use of CO + H_2 (syngas) chemistry in the industrial generation of bulk materials.[1–4] A predicted[5] theme of the current decade is the application of main-group organometallic compounds to the synthesis of higher value fine chemicals in smaller volume. Increasing interest has been shown in this area.[6–8]

There are numerous examples for the use of the carbonylation of amines by carbon monoxide in the synthesis of N-substituted formamides[9–11] and of N,N′-disubstituted ureas,[11–13] especially with the use of transition metal catalysts. Surprisingly, no methods based on carbonylation of amines has been described for the preparation of oxomalonamides prior to our recently reported synthesis, based on the reaction of CO with lithium amides.[14] Previously, we have reported the use of the same reaction for the synthesis of N,N-disubstituted formamides,[15] glyoxylamides, and hydroximalonamides.[16]

In spite of the great synthetic utility[6–16] of the carbonylation of lithium amides supportive mechanistic details have fallen into place only slowly. The limitations in our understanding of the chemistry of lithium amides stem, at least in part, from a shortage of structural information. This deficiency is being remedied rapidly, as solid-state[17–20] and solution[20–24] structures are elucidated. An expanded and critical theoretical approach (perhaps most notably from Schleyer,[25–27] Streitwieser,[27,28] and more

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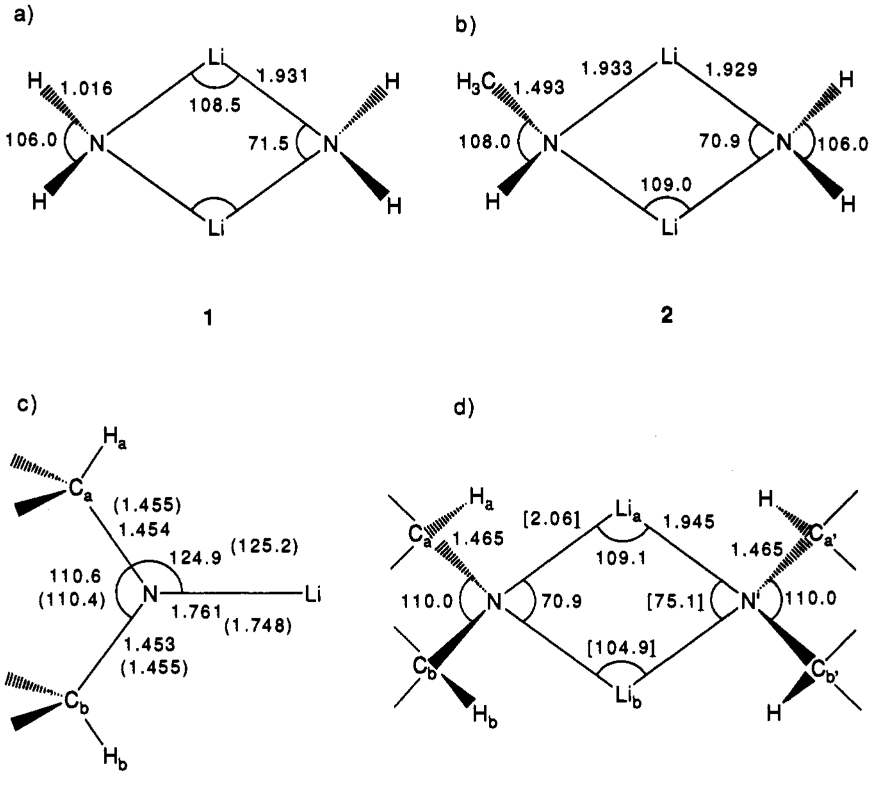
Table 1. Ab Initio Calculated Energies (au) and Heats of Formation ΔH° (kcal/mol), MNDO, and AM1 for the Various Intermediates

species	6-31G	6-31+G//6-31G	6-31+G*//6-31G	MP2/6-31+G*//6-31G	MNDO	AM1
3a	–141.036 897	–141.042 586	–141.097 374	–141.544 548	–4.87	16.03
4	–282.174 908	–282.181 840	–282.288 441	–283.184 473	–60.40	–10.90
5	–253.749 951	–253.757 722	–253.864 197	–254.610 273	–50.07	–20.64
6a	–366.431 852	–366.445 505	–366.604 256	–367.645 123	–64.92	–26.05
6b	–366.421 553	–366.432 381	–366.593 160	–367.636 251	–85.30	–51.04
6c	–366.376 076	–366.388 664	–366.554 869	–367.609 349	–81.30	–44.90
7	–620.321 647	–620.339 883	–620.578 009	–622.400 737	–152.48	–61.57
8	–394.803 232	–394.816 092	–394.965 093	–396.189 300	–32.71	–32.63
CO	–112.667 222	–112.671 505	–112.741 336	–113.028 209	–5.92	–5.68



1 **2**

3a **4**

Figure 1. Selected geometric parameters for species **3a** and **4** at the 6-31G level. 6-31+G values for species **3a** are in parentheses. Also included in Figure 1d are the X-ray experimental values for lithium diisopropylamide solvated by THF (see text). Values for structures **1** and **2** are calculated at 3-21+G level (refs 30 and 40).

recently Snaith[20a,29]) has contributed to the understanding of the peculiar organolithium compound structures.

The present work describes some theoretical calculations at the 6-31+G//6-31G and MP2/6-31+G*//6-31G levels of the structures of monomeric and dimeric lithium tetramethyl amides and of the intermediates formed in the carbonylation and double carbonylation reactions. To our knowledge, no previous studies on these reactions have been reported. The most closely related work is the McKee's MNDO and ab initio study (3-21+G basis set) of the reduction of formaldehyde by lithium methylamide,[30] and the MNDO calculations of solvated dialkylamides recently reported by Romesberg and Collum.[31]

Methods and Results

Standard ab initio molecular orbital calculations[32a] were carried out with the GAUSSIAN-88 system of programs.[32b] Stationary points on the potential energy surface were located at the Hartree–Fock level by use of gradient optimation procedures[33,34] (Berny optimization program) with the split-valence 6-31G basis set.[35,36] Improved energies were obtained as single point calculations employing a basis set with diffuse functions on nitrogen (6-31+G). Hydrogen p polarization functions were not included since they are expected to have only a minor effect on the calculated geometries and energies.[37] This is also expected for electron correlation effects and zero-point-energy corrections, as discussed below for the dimerization of lithium amide. Nevertheless, to test the relevance of electron correlation we have recalculated all the structures localized in the potential energy surface at the second-order Moller–Plesset (MP2)[38] level, using a basis set with d-type functions on heavy atoms[36] (MP2/6-31+G*//6-31G). Semiempirical MO calculations using AM1[39a] and

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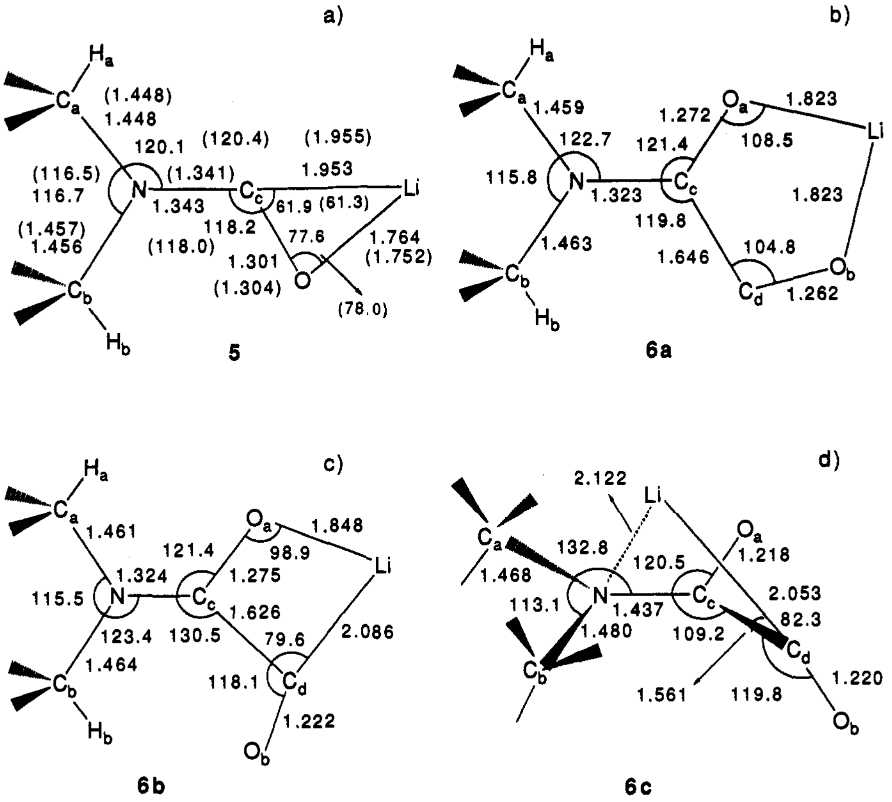

Figure 2. Selected geometric parameters for species **5** and **6** at the 6-31G level. 6-31+G values for species **5** are in parentheses.

MNDO[39b] methods implemented in the MOPAC (Version 6.0) system of programs[40] were also carried out for most of the structures. The complete results of the semiempirical calculations will be published elsewhere.[41]

Calculated ab-initio total energies and semiempirical heats of formation are presented in Table 1 for the reactants (CO and species **3**–**4**) and for some carbonylation intermediates (species **5**–**10**). Although full geometry optimizations were carried out for all species, for the sake of clarity only the skeletal parameters are considered here. Selected 6-31G geometrical parameters are given in Figures 1–3. Bond lengths are given in angstroms and angles in degrees. Total atomic charges for selected atoms of species **3**–**10** calculated at the 6-31+G//6-31G level (see the text) are gathered in Table 2. Some reaction energies are given in Table 3.

The 6-31G stationary points have been characterized by calculation of the Hessian matrix and successive analysis of the vibrational normal

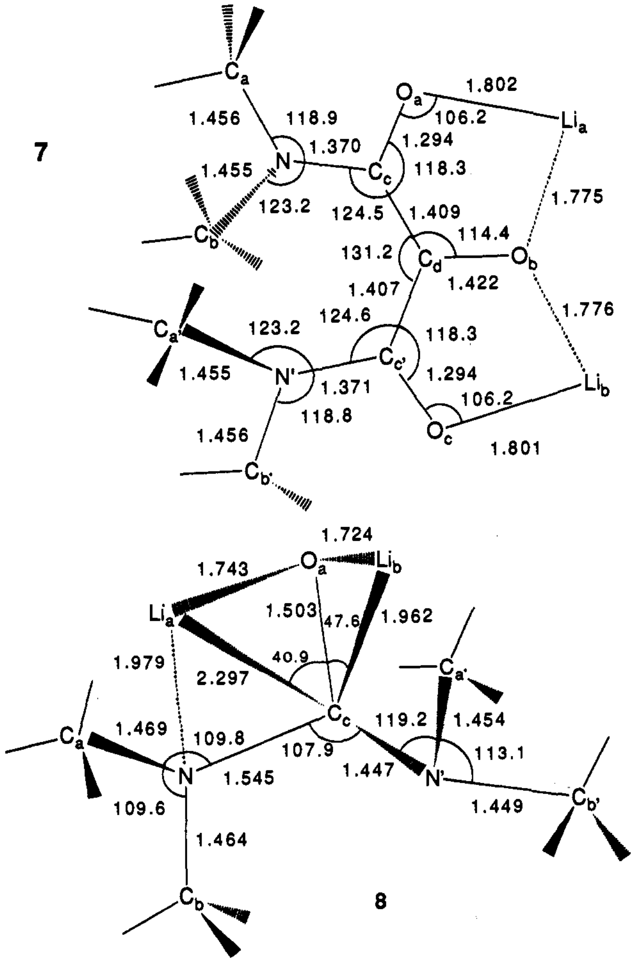

Figure 3. (Top) selected geometric parameters for species **7** at the 6-31G level. (Bottom) selected geometric parameters for species **8** at the 6-31G level.

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Table 2. Net Atomic Charges Calculated at the 6-31+G//6-31G Level to Selected Atoms for the Various Intermediates

	3a	**4**	**5**	**6a**	**6b**	**6c**	**7**	**8**
$q(\mathrm{N})$	–0.4434	–0.3913	–0.5163	–0.3254	–0.3372	–0.3638	–0.1866	–0.0715
$q(\mathrm{N'})$		–0.3912					–0.1843	0.0794
$q(\mathrm{Li_a})$	0.5089	0.3605	0.5330	0.6572	0.4428	0.3679	0.6075	0.5886
$q(\mathrm{Li_b})$		0.3604					0.6034	0.2492
$q(\mathrm{C_a})$	–0.4285	–0.4167	–0.3216	–0.3735	–0.3633	–0.3482	–0.3503	–0.3486
$q(\mathrm{C_b})$	–0.4281	–0.4167	–0.4335	–0.3653	–0.4503	–0.4663	–0.3610	–0.2336
$q(\mathrm{C_c})$			0.2450	0.5197	0.0070	0.5013	0.1536	–1.1131
$q(\mathrm{C_d})$				0.0294	0.7898	0.2871	0.2092	
$q(\mathrm{O_a})$			–0.6392	–0.7257	–0.6601	–0.5497	–0.7023	–0.5488
$q(\mathrm{O_b})$				–0.6847	–0.7146	–0.6919	–0.7608	
$q(\mathrm{O_c})$							–0.7026	
$q(\mathrm{O_d})$								
$q(\mathrm{C_a'})$		–0.4167					–0.3602	–0.3571
$q(\mathrm{C_b'})$		–0.4167					–0.3511	–0.2826
$q(\mathrm{H_a})$	0.1176	0.1386	0.2026	0.2474	0.2487			
$q(\mathrm{H_b})$	0.1180	0.1386	0.2491	0.2690	0.1861			
$q(\mathrm{C_c'})$							0.0929	

Table 3. Reaction Energies (kcal/mol)

reaction	6-31G	6-31+G//6-31G	6-31+G*//6-31G	MP2/6-31+G*//6-31G	MNDO	AM1
4 – 2(**3a**)	–63.5	–60.7	–59.1	–59.9	–50.7	–42.3
5 – (**3a** + CO)	–28.8	–27.4	–16.0	–23.5	–39.3	–31.0
6a – (**3a** + 2CO)	–38.0	–37.6	–15.2	–27.7	–48.2	–30.7
	–31.5	–29.4	–8.2	–22.1	–68.6[a]	–5.6[a]
6a – (**5** + CO)	–9.2	–10.2	0.80	–4.2	–8.9	0.3
					–24.7[b]	–19.3[b]
7 – (**5** + **6a**)	–87.8	–85.8	–68.8	–91.2	–37.5	–14.9
					–17.1[c]	10.1[c]
8 – (**5** + **3a**)	–10.3	–9.9	–2.2	–21.6	22.2	–28.0
7 – (**4** + 3CO)	–90.4	–90.1	–41.1	–82.6	–74.3	–33.6
8 – (**4** + CO)	24.4	23.4	40.6	14.7	33.6	–16.1
2(**5**) – (**4** + 2CO)	5.9	5.9	26.8	12.8	–80.6	–19.0

[a] **6b** – (**3a** + 2CO). [b] **6b** – (**5** + CO). [c] **7** – (**5** + **6b**).

modes. All the stationary points, although they exhibit unusual structures, have been recognized as true minima, since all vibrational frequencies are positive.

Results and Discussion

Reactant Structure. The propensity of organolithium compounds for association in the solid state,[17,18,20,29] in solution,[20,24] and even in the gas phase[42] is very well known. Seebach[17a] has recently published an enlightening and detailed discussion of mixed aggregates and mixed aggregation effects observed in the reactions of these compounds. In previous work, ab initio MO calculations have been carried out for the dimer of lithium amide, **1**,[20a,29b,43] and for the lithium amide:lithium methylamide mixed dimer, **2**[30] (shown in Figure 1a and 1b, respectively). To the best of our knowledge no previous ab initio calculations of lithium dimethylamide (monomer or dimer) have been reported. Although some controversy existed between early experimental[44] and theoretical[45] results, recent solid-state studies of lithium pyrrolidide complexes as well as ab initio MO calculations of lithium amide oligomers[20a] show that a ladder structure[44] is preferred to a stack structure.[45] Very recently, we reported the finding of the first [*amine·lithium amide*]$_4$ mixed aggregate, which shows a ladder solid structure by X-ray diffraction studies.[46] Furthermore, we have shown that the aggregation persists even in THF solution[16] and that carbonylation occurs within the aggregate.[24]

Table 1 gathers the 6-31G-optimized total energies for the monomer and dimer of lithium dimethylamide, whose geometries are shown as structures **3a** and **4** in Figure 1c and 1d, respectively. The skeletal framework is planar in the monomer, with one hydrogen of each methyl group in the plane, located in a syn position with respect to the N–Li bond. Although ammonia and alkylamines are pyramidal, the electropositive substituents in **3a** and **4** induce planarity at N.

The structures of two additional conformers of **3a** (not shown) have been optimized: one in which one methyl group is rotated, resulting in an *anti*-conformation of one of the planar hydrogens (species **3b**), and another in which both methyl groups have been rotated, giving species **3c** where both planar hydrogens are located *anti* to the lithium atom. According to the calculations, **3b** and **3c** are predicted to be more unstable than **3a** by only 3.9 and 6.7 kcal/mol, respectively. In all other species examined, it was found that structures with a planar methyl hydrogen (H_a) *syn* to the N–Li (or N–C_c) bond were the most stable. This may be a consequence of some extra stabilization arising from partial sharing of the positive charge of the lithium atom by the hydrogen. The charge distributions for selected atoms are given in Table 2 for all the species studied, with appropriate cautions about the significance of charge distributions derived from Mulliken population analysis. The hydrogen H_a is more positive than the other two methyl hydrogen atoms in all cases (not given in Table 2 for the sake of brevity).

Table 1 shows that the dimer is predicted to be 63.5, 60.7, and 59.9 kcal/mol more stable than the monomer at 6-31G, 6-31+G, and MP2/6-31+G*//6-31G levels, respectively. This result is very close to the best estimate (–62.5 kcal/mol) of the energy of dimerization of lithium amide recently calculated by Schleyer[25] at the 6-31+G*/6-31G*//6-31G* using diffuse functions on nitrogen, but not lithium (–65.1 kcal/mol) and with correlation (+0.6, on the basis of the 6-21G//3-21G-MP2/6-21G//3-21G difference) and zero point energy (+2.0) corrections. The LiNLi angle and the N–Li bond in **4** (Figure 1) are very close to those found for **1**[43] and for **2**.[30] X-ray studies[19,20,23,41,47–49] on complex derivatives of ($LiNH_2$) show the N–Li distances to vary from

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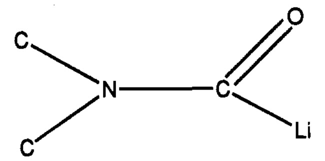
1.98 to 2.01 Å and the LiNLi and NLiN angles to lie within the 103–105° and the 75–77° ranges, respectively. The deviation of the theoretical bond length from experimental is then only 0.05 Å, and this can be attributed to additional ligand coordination.[25] The experimental values recently found in X-ray studies of the lithium diisopropylamide dimer solvated by THF[49] are shown in brackets in Figure 1d. The most stable structure calculated for **4** has the methyl substituents perpendicular to the plane formed by the N–Li bonds. This feature was previously found computationally for compounds **1**[39] and **2**[30] and in the solid-state structures of related lithium substituted amide dimers.[17,49]

It is notable that the AM1- and MNDO-optimized geometries for monomer and dimer compare satisfactorily with those obtained by higher-level MO calculations.[41] The MNDO version[40] used in this work (6.0) gives better results than the one previously used,[51] this probably reflects Thiel and Clark's[52] improved parameterization of MNDO for lithium. Thiel and Clark's parameters have been found to be remarkably successful in predicting the preferred mode of lithium complexation for other lithium compounds.[29a,30,53–55]

Several discussions on the degree of ionicity of the C–Li and N–Li bonds have been reported.[25,28,29,56] All experimental and theoretical studies show the N–Li bond to be more ionic than the C–Li bond. The dimer of lithium dimethylamide has a somewhat more distributed charge population than the monomer (Table 2): negative charges are located at both nitrogen atoms, and the positive charges are shared by the lithium and hydrogens atoms with a strong preference for the lithium atoms, as expected; charge excess is also observed at the methyl carbon atoms. Although the N–Li bond is essentially ionic, analyses of the highest occupied MO's suggest some multicenter covalent bonding involving lithium. As will be shown below, this feature has peculiar reactivity consequences in the reaction of these compounds with carbon monoxide and in the structural characteristic of the reaction intermediates. Even the preferred "perpendicular" (methyl groups located in a plane at 90° to the N–Li plane) over the "planar" (methyl groups in the N–Li plane) conformation observed for **4**, and previously found for **1** and for **2**, is a consequence of some N–Li overlap. The greater stability of the perpendicular over the planar arrangements was ascribed to the more favorable orientation of the nitrogen "lone pair" orbital toward the two adjacent lithium atoms.[43]

Intermediates Proposed for the Carbonylation Reaction. The classic migratory insertion reaction of carbon monoxide into a two-center, two electron metal–carbon bond is an extremely important transformation in stoichiometric and catalytic organometallic chemistry.[1–4,58] Nevertheless, it is not at present clear that a picture evolved solely from results on "soft" mononuclear transition-metal complexes is entirely accurate or complete in describing the rather drastic processes by which the several transformations of the CO molecule are occurring.[58] For the case of main-group organometallic reagents, the situation is even more obscure since very few mechanistic studies have been carried out yet.

The First Intermediate. For the reaction of lithium amides the "carbamoyl" structure **A** shown below is usually proposed as the intermediate resulting from insertion of CO into the reactant N–Li bond.[9,59,60] More recently, a contribution from a "carbenoid" structure has been also suggested.[16] To the best of our knowledge, no theoretical calculations on these intermediates have been carried out. MNDO semiempirical calculations on the unsubstituted[61] and dimethyl[51] carbamoyl anions have been recently reported, but we have found that inclusion of the metal atom is crucial in defining energetics and geometries in these reactions. Regarding the basis set for these systems, it was recently found that even the 3-21G level was reliable for qualitative trends in amide coordination with organolithium compounds.[57]



A

Figure 2a shows the 6-31G optimized geometry for **5**, the first carbonylation intermediate. Starting geometries such as the "carbamoyl" **A**, a planar "carbenoid" structure with the lithium bonded to oxygen or an alternative structure where the C_c–O and O–Li bonds are located in a plane perpendicular to the N–C_c–Li plane, all lead to the geometry displayed in Figure 2a. According to the calculations, **5** shows an η^2-coordinated lithium. This suggests an important contribution of an alkoxy carbene resonance form in the carbamoyl moiety. The C–Li (1.953 Å) and O–Li (1.764 Å) bond lengths (Figure 2a) indicate significant carbon–metal and oxygen–metal bonding. These lengths together with the linear arrangement of Li–C–N suggest that Li is more strongly bound to O than to C. These parameters, as well as the C–O length and the OCLi angle, satisfactorily compare with the corresponding values (1.907, 1.774, and 1.244 Å and 65.5°, respectively)[27] obtained for the formyllithium at the 6-31+G* level.

The calculated structure for intermediate **5** parallels those found in crystal structures of η^2 carbamoyl–metal complexes of actinide metals. Marks et al.[58] have reported the synthesis and X-ray study of stable bis(pentamethylcyclopentadienyl)organoactinide η^2 carbamoyls; the experimental values (e.g., C–O 1.276 Å; C–N 1.344 Å; U–O 2.342 Å; U–C 2.402 Å; UOC 77.0°; UCO 71.8° in $U[\eta\text{-}(CH_3)_5C_5]_2\{\eta^2\text{-}CO[N(CH_3)_2\}_2)$ are closely related to the geometry shown in Figure 2a. The actinide metals (U and Th) are much larger than the lithium atom, and the greater distance to the metal would result also in a larger O–C–M angle, as observed. One of the most interesting structural features of these complexes is the η^2-coordination of the carbamoyl ligands, also found in the calculated structure **5**. Another common feature is that the average M–O distance is significantly shorter than the M–C distance reflecting the "carbenoid" nature of the species. The experimental C–O bond lengths, as well as those calculated for compound **5**, are significantly longer than those reported for organic amides (1.212–1.225 Å)[62a,b] or for η^1 carbamoyls (1.214–1.25 Å)[62c,d] This indicates a significant perturbation of the carbonyl group. On the other hand, the C–N distance is not significantly different from that observed in the actinide compounds (typically 1.362 and 1.370 Å, respectively).[62]

In the carbamoyl crystals, the M, C, and N atoms are almost colinear (MCN: 170–175°), as also in the calculated structure for **5**. The high reactivity of lithium carbamoyls under the usual

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preparation conditions prevents their X-ray study with available techniques, but we think that the close correspondance observed between the solid-state structures of complexed actinide carbamoyls and the calculated lithium carbamoyl structures gives strong support to the reliability of the theoretical 6-31G calculations, for the present purposes. The calculated energy difference from the reactants (Table 3) is in accordance with the exothermicity of the reaction. The η^2-coordinated lithium in *N*,*N*-dimethylcarbamoyl, according to calculations, carries a smaller positive charge than observed in formyllithium (+0.85),[27] whereas the oxygen atom carries a weaker negative charge. As in formyllithium, the lithium–oxygen electrostatic stabilizes the η^2 structure **5**. As mentioned above, Li is more strongly bound to O than to C.

MO calculations of organolithium compounds using small basis sets can be questioned because they generally produce a large basis set superposition error[25,28] (BSSE). Inclusion of diffuse functions is thus considered essential for systems involving the accumulation of excess negative charge. Consequently, we have fully optimized the structures of species **3a** and **5** using a 6-31+G basis set that includes sp diffuse functions for all atoms except hydrogen. The 6-31+G geometrical parameters are shown in brackets in Figures 1c and 2a. The respective energies are −141.042 635 5 au and −253.757 796 au. It can be seen that inclusion of diffuse functions produces negligible changes in the geometrical parameters. Therefore, for these systems, the 6-31G geometries seem to be entirely adequate. In fact, it has been previously found that even the smaller basis 3-21+G minimizes the BSSE better than the 6-31G* basis set, which includes a set of d orbitals for all atoms except hydrogen.[47,48,56]

Table 1 shows the 6-31G, 6-31+G, and MP2/6-31+G*//6-31G energies calculated for the 6-31G-optimized structures. The electronic populations given in Table 2 are those calculated at the 6-31+G//6-31G level. As has been shown before, the correlation energy correction has minor effects for the dimer formation process. However, it is important to point out that for the formation of structure **5** the inclusion of d orbitals at SCF level modify the energetics of this process. The energy difference **5** − (**3a** + CO) changes from −28.8 and −27.4 kcal/mol at 6-31G and 6-31+G levels respectively, to −16.0 kcal/mol at 6-31+G* level. On the contrary, the inclusion of the electronic correlation (MP2/6-31+G*//6-31G) increases the energy difference to −23.5 kcal/mol which is close to the 6-31G and 6-31+G results. The same trend is also obtained for the remaining structures (see Table 3); i.e., energy differences obtained including electronic correlation approach those calculated at the 6-31G and 6-31+G levels. These results are analogous to those found by Kaufmann et al.[27] for the reaction of LiH with CO. In addition, the **5**-(**3a** + CO) energy difference estimated from the MP2/6-31G* results using 6-31G and 6-31+G geometries are practically identical. All these facts show that chemical conclusions obtained from 6-31G and MP2/6-31+G* results are the same. Comparison of ab-initio geometries with geometries given by semiempirical methods indicates an overall acceptable performance by semiempirical methods in reproducing the significant parameters, although in the AM1 geometry the LiCO angle and Li–O bond are too large.[41] The energetic difference between the intermediate and the reactants **5** − (**3a** + CO) given by the AM1 method (31.0 kcal/mol) is closer to that from 6-31G calculations than the value obtained by the MNDO (39.3 kcal/mol) method. An early MNDO calculation for the unsubstituted carbamoyl anion (ΔH_f = −23.3 kcal/mol) gives a structure closely similar to that of formamide,[61] again indicating the importance of including the metal atom in the calculations. (The MNDO ΔH_f of the dimethylanion is −27.3 kcal/mol).[51]

Further Reaction Intermediates. Coupling reactions typical of carbenoid structures were easily achieved with lithium acyl anions,[63] but no significant amounts of coupling products were detected in the carbonylation of lithium dialkylamides.[14–16] Similarly, coupling of actinide carbamoyls has not been effected even under forced conditions.[58] The large electron repulsion of the negative charges at nitrogen (Table 2) could prevent approach of two carbamoyl moieties at distances able to promote coupling.

The carbonylation of lithium dialkylamides also yields products containing two carbonyl groups in adjacent positions. These products can be formally postulated as arising from double carbonylation processes.[15] The reaction can lead to quantitative conversion to such products,[14] providing a highly convenient method for obtaining certain synthetic starting materials.[64] The precedents for double-carbonylation reactions are extremely limited,[65–67] and the scope of consecutive CO insertion seemed to be restricted to benzyl halides and their derivatives[64] until recently.[14–16] Limited early studies had been made concerning the equilibrium between acyl and alkylglyoxyl transition-metal complexes, and the double carbonylation reaction was considered thermodynamically unfavorable.[68] More recent research with palladium complexes provides additional evidence against a mechanism involving consecutive insertion of CO into the Pd–C bond.[64] No double carbonylation products were observed in the reaction of complexed actinide carbamoyls with CO.[58] Nevertheless, lithium carbamoyls under mild conditions can be carbonylated, providing a suitable route for the synthesis of alkyl-substituted glyoxalamides.[15]

The most stable structure of the intermediate arising from a double carbonylation process is shown as **6a** in Figure 2b. A planar arrangement of the heavy atoms provides strong stabilization to the intermediate, which was found to be 38 kcal/mol (6-31G and 6-31+G) and 28 kcal/mol (MP2/6-31G+G*//6-31G) more stable than the reactants (**3a** + 2CO). Calculations also show that the double carbonylation process is favorable: intermediate **6a** is more stable than **5** by 9.2 kcal/mol (6-31G) and 4.2 kcal/mol (MP2/6-31G+//6-31G), consistent with the high yield of double carbonylation observed in the reaction. Both relatively short O–Li bonds provide extra electrostatic stabilization by interactions of the metal with both negatively charged adjacent atoms, as well as the formation of a five-membered ring. The carbon atom bonded to nitrogen carries a significant positive charge (Table 2). It is worth noting (cautiously) that this intermediate exhibits the stronger positive charge on lithium observed throughout the present study. This result explains the rather peculiar effect of the ratio $[HNR^1R^2]/[LiNR^1R^2]$, observed in the reaction. In fact, a quantitative yield of products formally derived from **6a** is obtained when that ratio is 0.8, while a ratio = 0.2 gives a higher yield of products derived from **7**.[14,15] In light of the present calculations, it is clear that the more acidic lithium atom in intermediate **6a** is easily replaced by hydrogen in the presence of a proton donor like the free amine, preventing the further reaction between **6a** and **5** that produces intermediate **7**. The result is also consistent with the observed solvent effect: increasing polarity of the solvent favors formation of the more ionic intermediate **6a**.[15,16]

Another 6-31G stationary point **6b** has been found, and it is more unstable than species **6a** by only 6.5, 8.2, and 5.6 kcal/mol at 6-31G, 6-31+G, and MP2/6-31G+G* levels, respectively. The geometry shows a four-membered ring and a C=O double bond.

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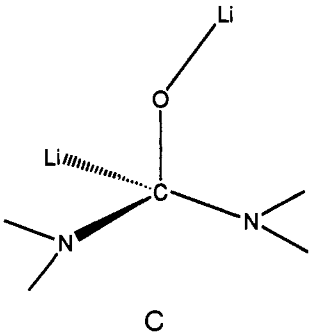
Remarkably, the MNDO and AM1 semiempirical methods give this structure as the most stable for the double carbonylation intermediate. A third structure, where both methyl carbon atoms are located almost perpendicularly to the NCCLi central ring, is also given by semiempirical methods.[41] This structure (similar to **6c**, Figure 2d) is only 4 and 6 kcal mol^{-1} more unstable than **6b**, by methods MNDO and AM1, respectively. Starting from the geometry given by semiempirical methods, the 6-31G structure **6c** was localized, but it is much more unstable than **6a** and **6b** (see Table 1).

Reaction between intermediates **5** and **6** produces a new intermediate which is the precursor for one of the main reaction products. 6-31G calculations gave a highly stabilized structure in which both lithium atoms are simultaneously coordinated to two oxygens (species **7**, Figure 3 (top)). The planar arrangement of the main heavy-atom framework, the close structural correspondence between the fragments around C_d, and the relatively short O–Li lengths all contribute to a very stable geometry for **7**. The low energy of **7** (Table 1) is probably responsible for the reaction progressing in the direction of **7** at low [amine]:[amide] ratio, thus giving high yields of hydroxymalonamides. The relative 6-31G and 6-31+G energies shown in Table 3 for **7** in respect to (**4** + 3CO) and (**5** + **6**) are exothermic, about −90 and −87 kcal/mol, respectively, and are also consistent with this result. The MP2 results, −82.6 kcal/mol for **7** – (**4** + 3CO) and −91.2 kcal/mol for **7** – (**5** + **6a**), follows the same trend. The AM1 and MNDO methods gave essentially similar geometries for the skeletal planar arrangement and for the spatial position of all atoms, although the O–Li lengths are longer than those shown by ab initio[41] calculations (Figure 3 (top)).

Although alkyl formamides can be proposed formally to arise from hydrolysis of intermediate **5**, which for some time was considered to be "an unexplained island of stability in the area of acyl anions";[70] we have shown that the real precursor for alkyl formamides is a lithium tetralkylurea dianion.[15,16] Calculations for this intermediate give the peculiar geometry shown as **8** in Figure 3 (bottom), with a central tetrahedral carbon C_c and a very small OC_cLi_b angle. Both O–Li lengths are very similar, and the Li_a atom is located at a relatively close distance to N. All the other bond angles are within reasonable values for tetrahedral atoms. The rest of the geometrical parameters are also in standard ranges. On the contrary, AM1 and MNDO methods gave a geometry more in accord with that expected, showing an atomic arrangement like C.



C

The atomic charges in **8** given by 6-31+G//6-31G are mechanistically suggestive (see Table 2). This intermediate exhibits a less negative oxygen than all the previous intermediates, and a highly negative C_c atom, indicating the carbanion character of this species. The lithium bound to this carbon is also the least positive of any lithium in all the complexes studied. This is probably due to the short distance to oxygen in a η^2 coordination. The high electron density on C_c makes it prone to oxidation and explains why **8** is easily transformed into urea by a feeble treatment with oxygen at atmospheric pressure and room temperature.[14] The lithium carbonylated intermediates are usually formulated as carbanionic but the present calculated finding that intermediates **6**, **7**, and **8** show carbenelike structures opens an interesting synthetic route for these intermediates. They also rise a challenging novelty for crystallographers; the X-ray structure of the first lithium halogen carbenoid has been recently reported.[71]

Regarding the mechanism of reaction, single electron transfer mechanisms have been proposed in reactions of organolithium compounds,[72] and we have recently reported evidence that single electron transfer is the first step in the reaction of aryllithiums with carbon monoxide.[63] Nevertheless, no evidence of radicals has been detected in the carbonylation of dilithium alkyl amides. The reaction seems to proceed by polar pathways consistently with the calculated structures of the intermediates.

In the addition of organolithiums to carbonyl groups the trajectory of attack by the nucleophile has been the subject of many previous discussions.[26,27,30,73] A detailed exploration of the potential energy surface of the smallest system, HLi/CO, at rather high levels has been recently published.[27] The effect observed for the addition of donor bases to the reaction media[14,15] suggests that coordination of CO with the lithium atom is the first step in the reaction and **4**. Calculations of the trajectoy of attack by CO to the dimeric lithium amide are in progress.

Conclusions

The structure of the first intermediate in the reaction of lithium dialkylamides with CO has been shown to be a lithium oxycarbene, instead of the carbamoyl reported in the literature. This complex easily reacts with another CO to produce a second intermediate where the lithium is η^2 coordinated to both oxygens. The calculated charge distribution explains the peculiar effect of the presence of free amine in the reaction media, which produces a high yield of glyoxylamides. The double carbonylation is predicted to be a thermodynamically favorable process, −38 kcal/mol (6-31G and 6-31+G) and −28 kcal/mol (MP2/6-31G+G*) in contrast to previous reports. Coupling of the two intermediates produces the highly stabilized dilithium tetramethylhydroxymalonamide (by −88, −86, and −91.2 kcal/mol at 6-31G, 6-31+G, and MP2/6-31+G* levels, respectively). The dilithium tetraalkylurea dianion is the real precursor of substituted formamides; calculations predict its easy oxidation to substituted ureas. The calculated finding that the three carbonylated lithium intermediates show carbenelike structures opens an interesting synthetic route for this reaction.

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