

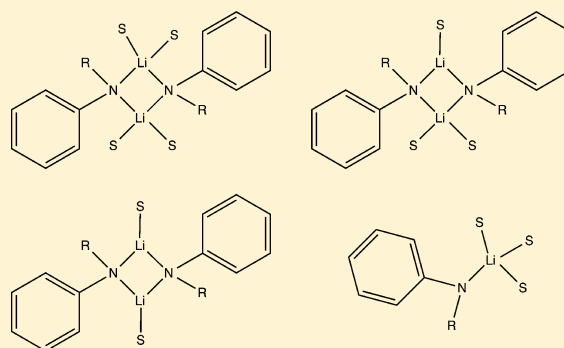
Structures of Lithium *N*-Monosubstituted Anilides: Trisolvated Monomer to Tetrasolvated Dimer

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S Supporting Information

ABSTRACT: Crystal structure determination of lithiated *N*-methylaniline with a variety of ligands, including tetrahydrofuran, methyltetrahydrofuran, *trans*-2,5-dimethyltetrahydrofuran, dimethoxyethane, tetrahydropyran and *N,N*-diethylpropionamide, reveals a common Li–N–Li–N four-membered-ring dimeric structure motif. A progression of solvation from tetrasolvated dimer (PhNMeLi·S₂)₂ through trisolvated dimer to disolvated dimer (PhNMeLi·S)₂ was observed by increasing the steric hindrance of the ligand. Solid-state structures of several other lithium *N*-alkylanilides solvated by tetrahydrofuran are also reported. When the methyl group of *N*-methylaniline is replaced by an isopropyl or a phenyl group, trisolvated monomers are formed instead of dimers. Interestingly, the solid-state structure of lithiated *N*-isobutylaniline in tetrahydrofuran is a trisolvated dimer while that of lithium *N*-neopentylanilide is a disolvated dimer.



INTRODUCTION

Lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium tetramethylpiperidine (LiTMP) are widely employed to abstract protons from various substrates.¹ The reactivities and aggregation states of LDA, LiHMDS, and LiTMP have been extensively studied.^{1,2} Although lithiated secondary anilines are also useful in deprotonation reactions,³ knowledge of their reactivities, aggregation states, and solvation states is not as well established as for LDA, LiHMDS, and LiTMP. More importantly, lithium phenolates display similar behavior as lithium enolates and are often used as models of enolate.⁴ Analogously, lithium anilides are used as models of lithium enamides, which are important substitutes for enolates.⁵

In 1987, Jackman reported a series of NMR experiments to evaluate the solution structures of several lithium anilides, including indolide, 2-methylindolide, methylanilide, tetrahydroquinolide, isopropylanilide, and butylanilides, in ethereal solvents.⁶ The results suggested that the aggregation state of lithium anilides depends on steric factors. Jackman proposed that different lithium anilide aggregates exist in equilibrium as depicted in Scheme 1, where A represents anilide and S represents solvent. Depending on the steric hindrance of the anilide, only one or two aggregates coexist. It is noteworthy that no evidence for the existence of aggregate 2 was proposed. Moreover, definitive evidence for the existence of a trisolvated monomer corresponding to aggregate 5 is rare. Collum and co-

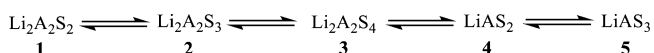
workers carried out thorough studies of lithium diphenylamide.⁷ These studies led to the conclusion that lithium diphenylamide exists as a dimer and a monomer in equilibrium with each other in tetrahydrofuran (THF). However, the solvation state of the monomeric aggregate remained obscure.

In an attempt to obtain a greater understanding of the structure of lithium anilides as well as to augment the previous work done by Jackman and Collum, we synthesized and crystallized a series of lithium *N*-alkylanilides in ethereal solvents. The crystal structures of 14 lithium anilides were obtained and are reported. These structures confirm that the aggregation and solvation states are highly dependent on the steric factors of both the anilide and the solvent. These results provide not only vital details of the structures of previous species observed in solution but also important solvation information previously undetermined about the lithium anilides.

RESULTS AND DISCUSSION

Tetrahydrofuran-Tetrasolvated Dimers of Various Lithium Anilides. The THF solvates of lithiated *N*-methylaniline (6), *N*-ethylaniline (7), indoline (8), and tetrahydroquinoline (9) were determined by X-ray diffraction analyses to be tetrasolvated dimers. As depicted in Scheme 2, 1 equiv of *n*-butyllithium (*n*-BuLi) was added to the anilides dissolved in pentane to generate yellow precipitates. These precipitates dissolved in THF. Storing the resulting solutions at –20 °C overnight led to crystals suitable for X-ray crystallography.

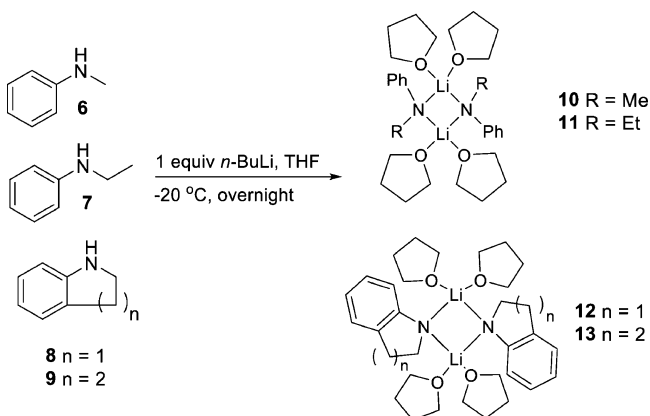
Scheme 1. Equilibrium of Lithium Anilide Aggregates (1–5)



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Scheme 2. Preparation of THF-Tetrasolvated Lithium Anilides **10**, **11**, **12**, and **13**



A few crystal structures of tetrasolvated lithium secondary amides have been reported.⁸ The newly obtained crystal structures of THF-solvated lithium *N*-methylanilide (**10**), lithium *N*-ethylanilide (**11**), lithium indolinide (**12**), and lithium tetrahydroquinolide (**13**) are depicted in Figures 1, 2,

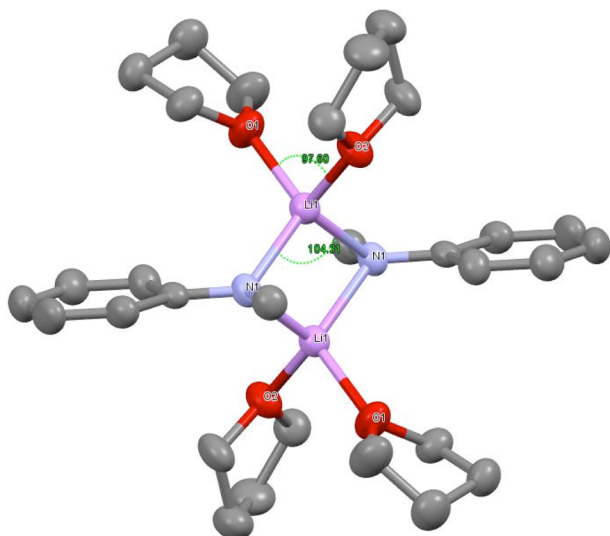


Figure 1. Crystal structure of THF-solvated lithium *N*-methylanilide (**10**). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

3, and **4** as dimers having a planar Li_2N_2 core with tetracoordinate lithium atoms. All four lithium anilide dimers adopt a structure in which the phenyl groups of the anilides are *trans* to each other, as illustrated in Scheme 3. The N-Li-N angles within the Li_2N_2 core are very similar for all four structures ($103.3\text{--}104.3^{\circ}$); however, the O-Li-O angles are significantly different (see Figures 1–4. The O-Li-O angles in **10** and **12** are 97.6° and 98.6° , respectively. The O-Li-O angle in **13** is 95.3° , whereas the corresponding angle in **11** is 92.4° , which is significantly smaller than those in **10** and **12**. Since the terminal methyl group of **11** points away from the plane shared by the phenyl and methylene groups of the *N*-ethylanilides, as shown in Figure 2, we ascribe the relatively small O-Li-O angle in **11** to the steric effect of the ethyl group.

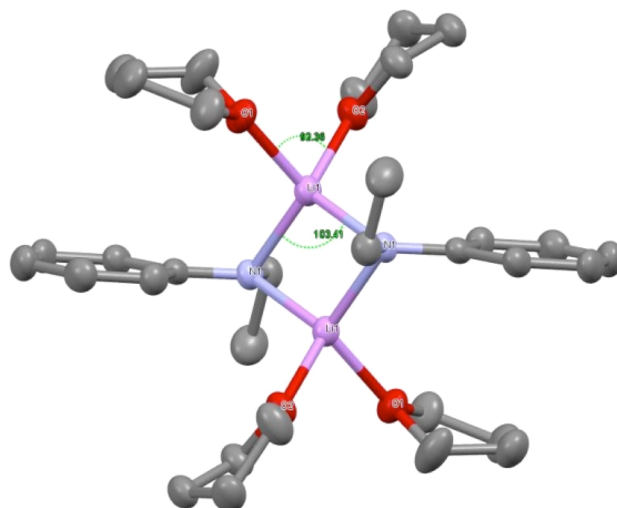


Figure 2. Crystal structure of THF-solvated lithium *N*-ethylanilide (**11**). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

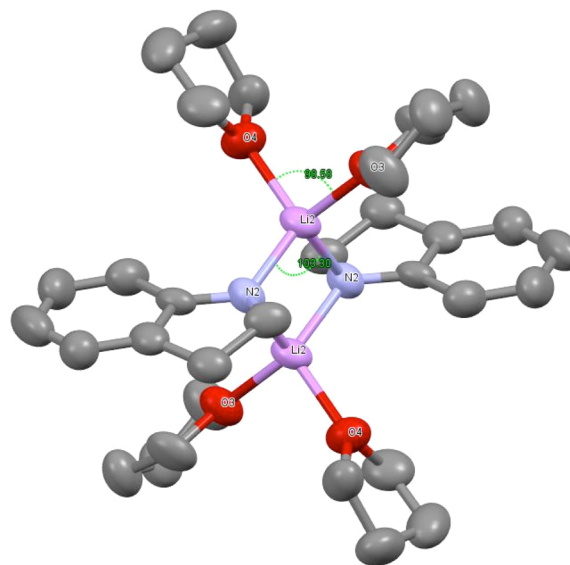


Figure 3. Crystal structure of THF-solvated lithium indolinide (**12**). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Tetrahydropyran-, Methyltetrahydrofuran-, and *N,N*-Diethylpropionamide-Tetrasolvated Dimers of Lithium *N*-Methylanilide. Crystals of tetrahydropyran (THP)-, 2-methyltetrahydrofuran (MeTHF)-, and *N,N*-diethylpropionamide (DEPA)-solvated lithium *N*-methylanilide were prepared using the same method as previously described. As illustrated in Figures 5, 6, and 7, the solid structures of THP-solvated lithium *N*-methylanilide (**14**), MeTHF-solvated lithium *N*-methylanilide (**15**), and DEPA-solvated lithium *N*-methylanilide (**16**) are all tetrasolvated dimers. These are similar to the structure of THF-tetrasolvated lithium *N*-methylanilide in Figure 1. The two *N*-methylanilides lie nearly on the same plane and adopt the *trans* structure as previously described.

The O-Li-O angle in dimer **15** is 92.3° , which is significantly smaller than that in structure **10** and nearly the same as the O-Li-O angle in structure **11**. We attribute the compression of the O-Li-O angle to the steric interaction of

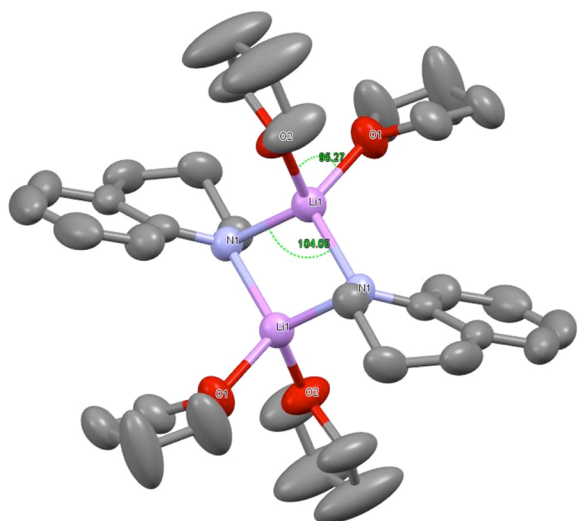


Figure 4. Crystal structure of THF-solvated lithium tetrahydroquinolide (13). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Scheme 3. The *trans* Structure of Lithium Anilides 10, 11, 12, and 13

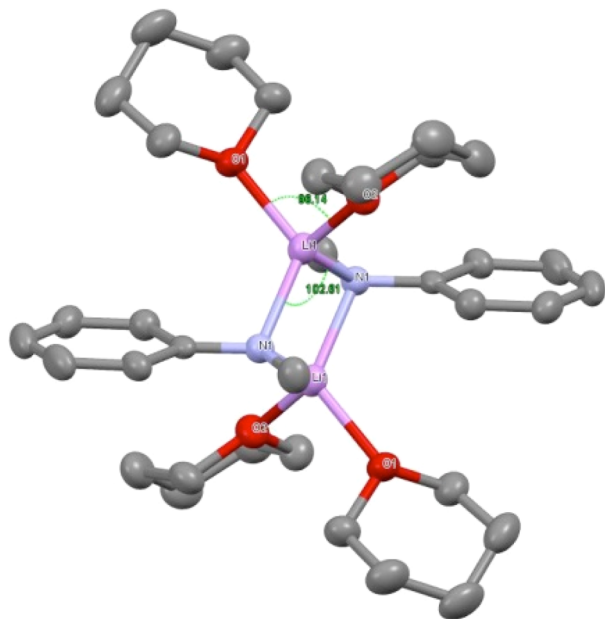
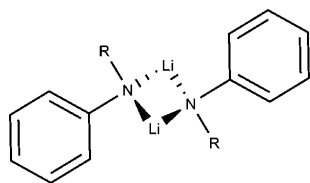


Figure 5. Crystal structure of THP-solvated lithium *N*-methylanilide (14). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

the methyl group of MeTHF with the anilide. As illustrated in Figure 6, the methyl groups of all four MeTHF molecules point away from the plane shared by the two *N*-methylanilide molecules.

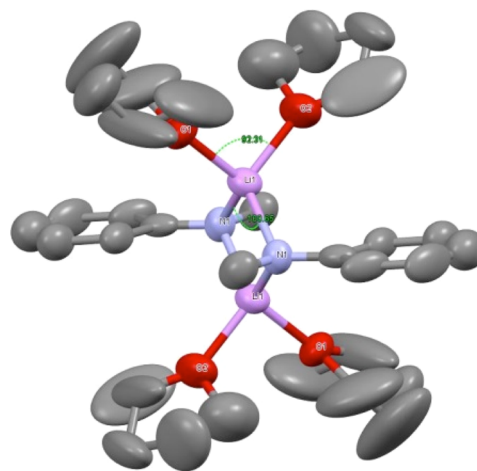


Figure 6. Crystal structure of MeTHF-solvated lithium *N*-methylanilide (15). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

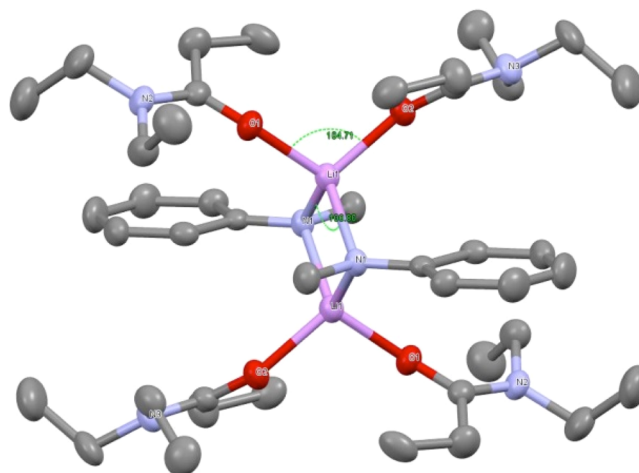


Figure 7. Crystal structure of DEPA-solvated lithium *N*-methylanilide (16). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

In the crystal structure of 16, the dimeric lithium *N*-methylanilide is solvated by four unenolized DEPA molecules. As expected, the oxygen atom coordinates to the lithium instead of the nitrogen atom of the amide group. The O–Li–O angle is 104.7°, which is significantly larger than that in structure 10 because the steric hindrance around the carbonyl oxygen is less than the hindrance around the etheral oxygen of THF. Structure 16 also provides some insight into the basicity of lithium *N*-methylanilide in that DEPA in this complex remains unenolized and no deprotonation of the coordinating solvent takes place.

Dimethoxymethane-Tetrasolvated Dimers of Two Lithium *N*-Alkylanilides. In 1987, Snaith and co-workers reported the crystal structure of an *N,N,N',N'*-tetramethylethylenediamine (TMEDA)-disolvated lithium *N*-methylanilide dimer.⁹ Later, Schleyer and co-workers reported the solid-state structure of TMEDA-disolvated lithium indolate dimer.¹⁰ The TMEDA-disolvated lithium *N*-diphenylamide dimer was reported by Mulvey et al. in 2009.¹¹ Since dimethoxymethane (DME) is also a bidentate ligand, we anticipated that the solid-state structures of DME-solvated lithium anilides would adopt the same motif as the TMEDA solvates. However, the solid-

state structure of TMEDA-solvated LiHMDS differs from that of DME-solvated LiHMDS. The former is a monosolvated monomer while the latter is a η^1 -DME-disolvated dimer.¹² Therefore, we attempted to crystallize DME-solvated lithium *N*-methylanilide and *N*-ethylanilide to evaluate the solvation state of the lithium with DME.

As depicted in Figures 8 and 9, the crystal structures of DME-solvated lithium *N*-methylanilide (17) and lithium *N*-

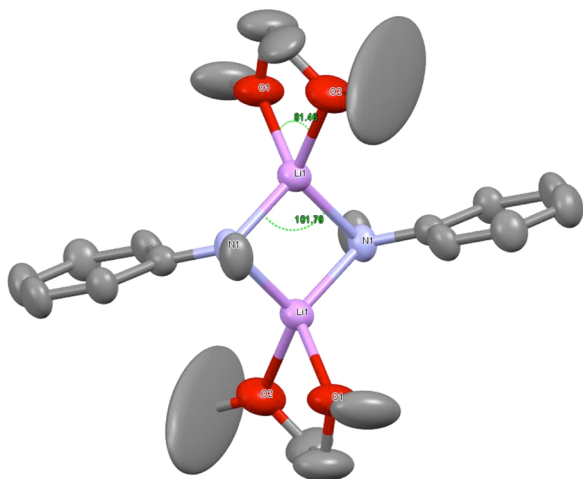


Figure 8. Crystal structure of DME-solvated lithium *N*-methylanilide (17). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

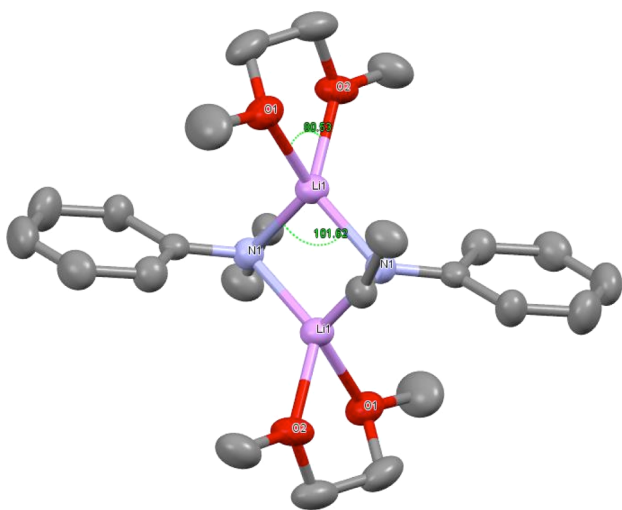


Figure 9. Crystal structure of DME-solvated lithium *N*-ethylanilide (18). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

ethylanilide (18) adopt the same solvation pattern as TMEDA-solvated lithium *N*-methylanilide. Both are η^2 -DME-disolvated dimers with a planar Li_2N_2 core in which the lithium atoms are tetracoordinate. Both dimers adopt the *trans* structure depicted in Scheme 3. Similar to structure 11, the terminal methyl groups in structure 18 also point away from the plane shared by the phenyl and methylene groups of the *N*-ethylanilides. However, the O–Li–O angle in structure 18 is very similar to that in structure 17 because the steric hindrance of one DME molecule is significantly smaller than the hindrance of two THF molecules.

2,5-Dimethyltetrahydrofuran-Disolvated Dimer of Lithium *N*-Methylanilide. To assess the effect of steric hindrance of the solvent on the aggregation and solvation states of lithium *N*-methylanilide, we crystallized 2,5-dimethyltetrahydrofuran (DMTHF)-solvated lithium *N*-methylanilide using the method described previously. The crystal structure (Figure 10)

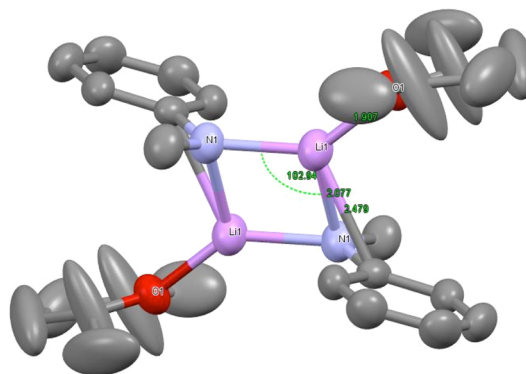


Figure 10. Crystal structure of DMTHF-solvated lithium *N*-methylanilide (19). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

is a DMTHF-disolvated dimer analogous to numerous disolvated dimeric lithium amide structures as well as the structures of diethyl ether-disolvated *N*-(2,2-dimethyl-*L*-methylene-*propyl*)-*N*-lithiobenzeneamine and THF-solvated lithium dipentafluorobenzeneamide.¹³ The phenyl groups of the methylanilides are *trans* to each other in a distorted plane. The lithium atoms in the Li_2N_2 core bind to the nitrogen of the anilide and are in close proximity (2.47 Å) to the *ipso* carbon of the benzene ring. This short distance suggests the existence of auxiliary coordination in this complex. Additional examples of similar short *ipso* carbon–Li distances in related crystal structures are known.¹⁴

Tetrahydrofuran-Trisolvated Monomers of Lithium *N*-Isopropylanilide and Lithium *N*-Diphenylamide. To assess the effect steric hindrance of the alkyl group on the aggregation and solvation states of lithium *N*-alkylanilides, crystals of THF-solvated lithium *N*-isopropylanilide and lithium *N*-diphenylamide were grown. As illustrated in Figures 11 and

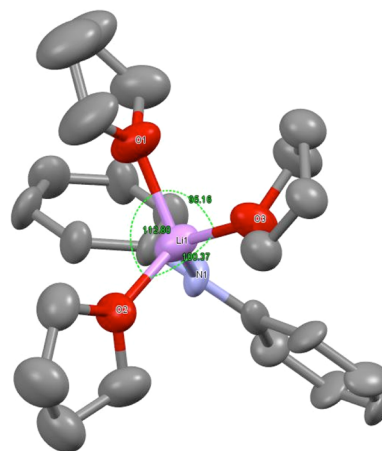


Figure 11. Crystal structure of THF-solvated lithium diphenylamide (20). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

12, the crystal structures are THF-trisolated monomers similar to the solid-state structure of the THF-trisolated monomer of

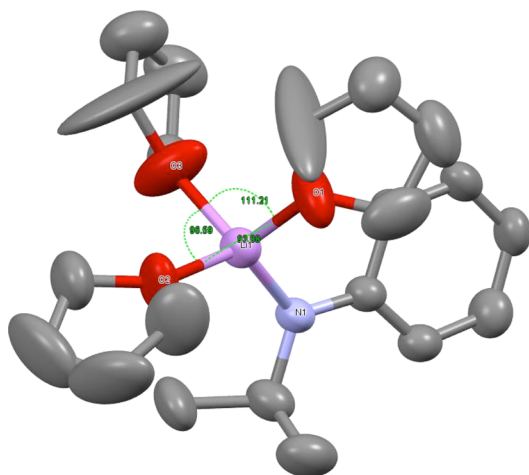
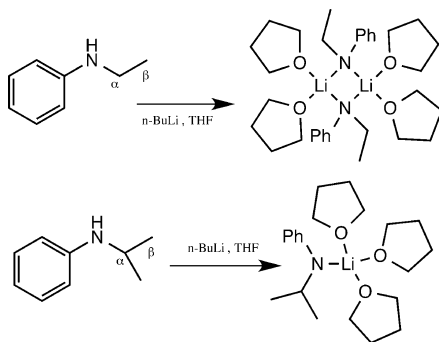


Figure 12. Crystal structure of THF-solvated lithium *N*-isopropylanilide (**21**). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

lithium phenothiazide reported by Cragg-Hine and co-workers.¹⁵ The three O–Li–O angles in structure **20** are 95.2°, 100.4°, and 112.8°, whereas the corresponding O–Li–O angles in structure **21** are 93.9°, 96.6°, and 111.2°. The values suggest that the isopropyl group is slightly larger than the phenyl group. The THF-trisolated monomers provide an important clue for the solvation state of lithium diphenylamide in THF.^{5b} These structures illustrate that the formation of a THF-trisolated monomer occurs upon addition of a methyl group to the α -carbon of *N*-methylanilide (Scheme 4).

Scheme 4. Branched Chains of *N*-Alkylanilines



Tetrahydrofuran-Trisolated Dimer of Lithium *N*-Isobutylanilide and Tetrahydrofuran-Disolvated Dimer of Lithium *N*-Neopentylanilide. To further assess how the size of the alkyl group in lithium *N*-alkylanilides influences the aggregation and solvation states of lithium *N*-alkylanilides, we synthesized and crystallized THF-solvated lithium *N*-isobutylanilide and lithium *N*-neopentylanilide as representative exemplars of increasingly larger substrates.

The solid-state structure of THF-solvated *N*-isobutylanilide is an unusual trisolated dimer, as depicted in Figure 13. The Li_2N_2 core is not planar, and the phenyl groups of the anilides are *cis* to each other. There are two different lithium atoms, one tricoordinate and the other tetracoordinate. Moreover, the two *cis* isobutyl groups bend in the same direction toward the

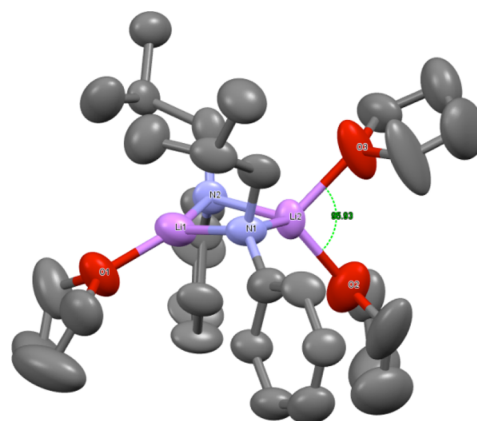


Figure 13. Crystal structure of THF-solvated lithium *N*-isobutylanilide (**22**). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

tricoordinate lithium atom, thereby providing enough space for the two THF molecules to bind with the other lithium atom in the opposite direction. The solid-state structure of this trisolated dimer supports the existence of aggregate **2** proposed by Jackman.^{4a}

Further increasing the steric hindrance of the β -carbon of the alkyl group leads to the formation of the THF-disolvated dimer. As depicted in Figure 14, THF-solvated lithium *N*-neo-

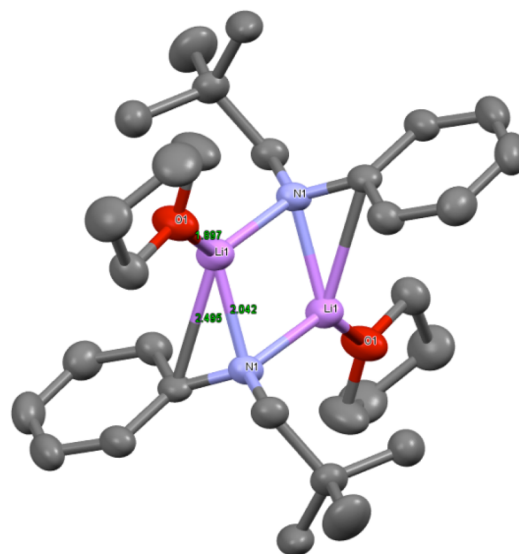


Figure 14. Crystal structure of THF-solvated lithium *N*-neopentylanilide (**23**). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

pentylanilide is a disolvated dimer similar to the DMTHF-disolvated dimer of lithium *N*-methylanilide. In 2001, Lappert and co-workers reported the crystal structure of the diethyl ether-disolvated dimer of lithium *N*-neopentylanilide.¹⁶ In the THF-disolvated dimer depicted in Figure 14 and the Lappert compound, the phenyl groups of the anilides are *trans* to each other in a distorted plane and the two neopentyl groups point in opposite directions.¹⁷ Similar to the structure of **19**, the lithium atoms in the structure of **23** and the analogous diethyl ether solvate display a short contact with the *ipso* carbon of the benzene ring (~ 2.5 Å).

Taken together, these results suggest that the increase in the steric hindrance of the β -carbon of the alkyl group affects the solvation state significantly. While the solid-state structures of lithium anilides **11**, **22**, and **23** are all dimeric, the solvation state changes from tetrasolvated in the structure of **11** to disolvated in the structure of **23** with the increase in the steric hindrance of the β -carbon of the alkyl group.

A summary of the structures reported herein is shown in Table 1. It is clear that the solvation and aggregation states of the complexes depicted exhibit a correlation with the steric

requirements of their components. It remains to be determined whether there is also a discernible correlation between the structures of these different complexes and their reactivities.

CONCLUSION

It is clearly evident that the solid-state structures of lithium *N*-alkylanilides strongly depend on the steric factors of both the alkyl group and the solvating solvent. With sterically unhindered alkyl groups, lithium *N*-methylanilide, lithium *N*-ethylanilide, lithium indolide, and lithium tetrahydroquinolide crystallize as tetrasolvated dimers in THF. An increase in steric hindrance of the α -carbon of the alkyl group alters the aggregation state to a monomer in THF. This is evident in the solid-state structures of the THF-trisolvated monomers of lithium diphenylamide and lithium *N*-isopropylanilide. However, with an increase in the steric hindrance of the β -carbon, the solvation state changes instead of the aggregation state. The crystal structure of THF-solvated lithium *N*-isobutylanilide is a trisolvated dimer, supporting this conclusion. Moreover, a further increase in the steric hindrance of the β -carbon leads to the formation of a THF-disolvated dimer, as in the case of THF-solvated lithium *N*-neopentylanilide.

The size of the coordinating solvent alters the solvation state of the dimeric lithium *N*-methylanilide. With relatively unhindered coordinating solvents, the solid-state structures of lithium *N*-methylanilide are all tetrasolvated dimers in THF, THP, DEPA, and MeTHF. The crystal structures of lithium *N*-methylanilide and lithium *N*-ethylanilide with relatively unhindered coordinating DME, which is a bidentate ligand, are also disolvated dimers; however, the lithium atoms are tetracoordinate, identical to that of the tetrasolvated dimers. When sterically hindered DMTHF is used as the coordinating solvent, the structure motif changes to a disolvated dimer in the solid state.

Most importantly, these results confirm the existence of a trisolvated dimeric aggregate **2**. They also provide proof of the solvation states of these lithium anilides. We believe that these results provide some definitive insight into the relationship between substrate and/or solvent size and the aggregation and/or solvation state of the corresponding lithiated derivatives in a homologous series of *N*-substituted anilines ranging from trisolvated monomers through di-, tri-, and tetrasolvated tetramers.

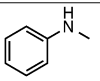

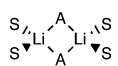
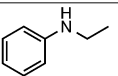

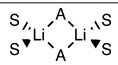
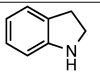

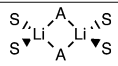
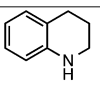

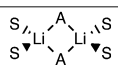
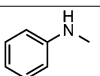

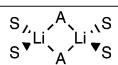
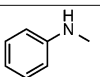

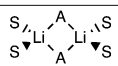
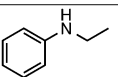
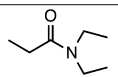
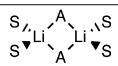
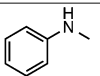
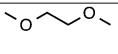
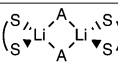
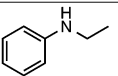
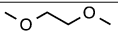
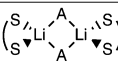
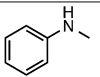

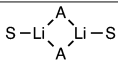
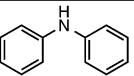


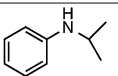


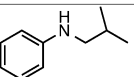

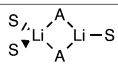
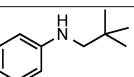

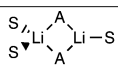
EXPERIMENTAL SECTION

Synthesis of *N*-Neopentylaniline. *N*-Neopentylaniline was synthesized by the method described by Lappert.¹⁵

General Procedure for the Crystallization of Solvated Lithium Amides. Etheral solvents were added to suspensions of the lithium amides to dissolve the suspended material. Although we did not measure the exact quantities of ethers added to these suspensions, we note that in all cases at least several equivalents of the ether solvent and frequently up to a volume equal to that of the nonetheral solvent was added.

Procedure for the Crystallization of THF-Solvated Lithium *N*-Methylanilide (10), Lithium *N*-Ethylanilide (11), Lithium Indolide (12), Lithium Tetrahydroquinolide (13), Lithium *N*-Isobutylanilide (22), and Lithium *N*-neopentylanilide (23). To a solution of the *N*-alkylaniline (0.9 mmol) in 1 mL of anhydrous pentane at 0 °C under an Ar atmosphere was slowly added 1 equiv of *n*-BuLi. The reaction mixture was allowed to stir at 0 °C until a light-yellow to orange precipitate formed. Anhydrous THF was then added slowly to the mixture until all of the precipitate dissolved into the solution and the solution became clear. XRD-quality crystals were grown when the solution was stored at –20 °C overnight.

Table 1. Summary of Observed Structure and Solvation Motifs

Compound	amine	solvent	motif	classification
10				Li ₂ A ₂ S ₄
11				Li ₂ A ₂ S ₄
12				Li ₂ A ₂ S ₄
13				Li ₂ A ₂ S ₄
14				Li ₂ A ₂ S ₄
15				Li ₂ A ₂ S ₄
16				Li ₂ A ₂ S ₄
17				Li ₂ A ₂ S ₄
18				Li ₂ A ₂ S ₄
19				Li ₂ A ₂ S ₂
20				Li ₁ A ₁ S ₃
21				Li ₁ A ₁ S ₃
22				Li ₂ A ₂ S ₃
23				Li ₂ A ₂ S ₃

General Procedure for the Crystallization of DEPA-Solvated Lithium *N*-Methylanilide (16) and DME-Solvated Lithium *N*-Ethylanilide (18). To a solution of the *N*-alkylaniline (0.9 mmol) in 1 mL of anhydrous pentane at 0 °C under an Ar atmosphere was slowly added 1 equiv of *n*-BuLi. The reaction mixture was allowed to stir at 0 °C until a light-yellow precipitate formed. DEPA or DME was then added slowly to the mixture until all of the precipitate dissolved into the solution and the solution became clear. XRD-quality crystals were grown when the solution was stored at –20 °C overnight.

General Procedure for the Crystallization of MeTHF-Solvated Lithium *N*-Methylanilide (15), DMTHF-Solvated Lithium *N*-Methylanilide (19), and THF-Solvated Lithium Diphenylamide (20). To a solution of the *N*-alkylaniline (0.9 mmol) in 1 mL of anhydrous pentane at 0 °C under an Ar atmosphere was slowly added 1 equiv of *n*-BuLi. The reaction mixture was allowed to stir at 0 °C until a light-yellow or purple precipitate formed. THF or MeTHF or DMTHF was then added slowly to the mixture until all of the precipitate dissolved into the solution and the solution became clear. The clear solution was then stored at –50 °C in a freezer, and XRD-quality crystals were grown at –50 °C overnight.

General Procedure for the Crystallization of THP-Solvated Lithium *N*-Methylanilide (14) and DME-Solvated Lithium *N*-Methylanilide (17). To a solution of *N*-methylaniline (0.05 g) in 2 mL of THP or DME at room temperature under an Ar atmosphere was added 1 equiv of *n*-BuLi. The resulting solution was shaken vigorously and then stored at room temperature, and XRD-quality crystals were grown overnight.

General Procedure for the Crystallization of THF-Solvated Lithium *N*-isopropylanilide (21). To a solution of *N*-isopropylaniline (135 mg, 1.0 mmol) in 1.5 mL of anhydrous mixed solvent (heptane/THF 1:2) at 0 °C under an Ar atmosphere was slowly added 1.1 equiv of *n*-BuLi. The reaction mixture was allowed to stir at 0 °C for 5 min and then cooled to –78 °C until the whole solution was frozen. The sample was stored at –50 °C overnight and then at –20 °C until nice-shaped crystals were observed. The crystal-growing process took several days.

■ ASSOCIATED CONTENT

■ Supporting Information

Supplemental crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 958136–958146 and 958151–958153 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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