motions of guest and host. The changes in T_1 times as guest binds to host for the *R* enantiomer are larger than for *S*, again indicative of tighter *R* binding. The changes in inter- and intramolecular NOEs were also measured. Upon complexation, the same NOEs exist as in the free state but there is a reduction in the percent enhancement, again with the *R* tryptophan having the larger changes. An intermolecular NOE between tryptophan and cyclodextrin reveals the tryptophan aromatic H_4 to be near the cyclodextrin's H_3. The H_3 proton is on the interior of the macrocycle pointing in toward the cavity. A small NOE of similar magnitude for *R* and *S* enantiomers was found.

Gas-phase molecular simulations reveals that (*R*)-tryptophan forms a larger number of hydrogen bonds than does (*S*)-tryptophan, but more interestingly, it forms a larger number of multiple-contact hydrogen bonds. The number and location of intermolecular hydrogen bonds reveal three features. First, both complexes are highly localized in spite of weak intermolecular association. Second, the (*R*)-tryptophan forms twice as many hydrogen bonds as (*S*)-tryptophan, and the average intermolecular hydrogen bond energy for *R* is almost 3 kcal mol^{-1} more than for *S*. Third, the intermolecular hydrogen bonds arise from the tryptophan carboxylate oxygens and its indole N-H rather than from the ammonium group.

A previously proposed chiral recognition model is consistent with our results. Armstrong advocates four requirements for chiral recognition:[19] (a) an inclusion complex must form, (b) a tight fit of the included species with the host cavity must exist, (c) the stereogenic center should be able to form one strong interaction with the hydroxyl groups of the CD cavity entrance, and (d) the unidirectional 2- or 3-hydroxyl groups at the secondary face of the macrocycle are especially important for chiral recognition. Based on our experimental work, we find inclusion complexation but with the aromatic ring of the guest tilted and near the top of the cavity rather than deeply embedded in it along a C_6 symmetry axis. Point b is hard to measure, but we find the tryptophan molecules to be highly localized on the interior of the cavity effectively behaving like a tight fit. We propose, then, to modify this criterion to be a tight fit or a high localization of guest with host. The third requirement is met by the carboxylate, and the last point, interaction with the unidirectional 2- or 3-hydroxyl groups, has been fulfilled. This latter criterion appears to be the key element of differentiation although we recognize the CD as a whole to be chiral. The directionality of the secondary hydroxyl OH bond vectors is such that the indole N-H finds the host's secondary OH oxygens accessible for hydrogen bonding. The indole N-H of the *S* guest, in contrast, is impeded by the hydrogen atoms of those hydroxyl groups. This results in fewer hydrogen bonds, less multiple-contact hydrogen bonds, and less stabilization of the complex.

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Supplementary Material Available: Tables of chemical shifts and coupling constants for α-CD, ^1H and ^{13}C NMR spectra of α-CD, and ^{13}C proton-decoupled spectra of the aromatic and C_α, C_β regions (4 pages). Ordering information is given on any current masthead page.

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exo,exo-[1,3-Bis(trimethylsilyl)allyl]lithium–*N,N,N',N'*-Tetramethylethylenediamine Complex: Crystal Structure and Dynamics in Solution

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Abstract: The X-ray structure of the title compound (**1**·TMEDA) shows that the essentially symmetrical allyl anion moiety is perturbed by complexation with TMEDA in a twisted conformation. The NMR-observed symmetrization of both the allyl end carbons and all the TMEDA methyl groups at higher temperatures is best modeled by molecular orbital calculations when two mechanisms (ligand rotation and ligand twisting) are assumed. These are calculated to have nearly the same barrier and are in accord with the experimental value.

Introduction

Fraenkel, Chow, and Winchester recently[1] showed via ^{13}C and ^1H NMR, as well as a Saunders deuterium perturbation experiment,[2] that the *exo,exo*-[1,3-bis(trimethylsilyl)allyl]lithium–*N,N,N',N'*-tetramethylethylenediamine complex (**1**·TMEDA) in diethyl-d_{10} ether was "electronically symmetrical and exists in the exo configuration". The small ^{13}C NMR shift difference (0.48 ppm) between C(1) and C(3) of allyl in **1**·TMEDA and the large

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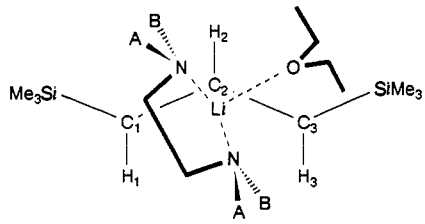
shift difference between the two $(CH_3)_2N$ groups (4.65 ppm) were attributed to dissymmetry of solvation about lithium (one TMEDA and one diethyl ether (DEE)) in the tight monomeric ion pair **1**·TMEDA·DEE.



1 · TMEDA · DEE

Above 150 K signal averaging of the C(1) and C(3) resonances and of the peaks for $(CH_3)_2N$ in bound TMEDA was observed. NMR line shape analysis suggested that these spectral changes might be due to the same dynamic process, the rotation of the solvated Li^+ moiety with respect to the allylic loop. The rate is 300 s^{-1} at 160 K with $\Delta H^{\ddagger}$ = 7.7 kcal/mol.[3] Most interestingly and pertinent to our results and conclusions discussed below, in *exo,exo*-[1,3-bis(trimethylsilyl)allyl]lithium (without TMEDA!) measured in THF-d_8, diethyl-d_{10} ether, or toluene-d_8 equivalent signals of C(1) and C(3) have been registered.[1]

NMR investigations of the parent allyllithium in THF revealed likewise an unsymmetrical species[5] which turned out to be a dimer.[5e] In the solid state, allyllithium–TMEDA consists of polymeric chains, in which the lithium cations connect the terminal carbon atoms of different unsymmetrical allyl units.[6a] When allyllithium is unsymmetrically coordinated with the tridentate ligand *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA), the lithium is also displaced from the central position toward one of the terminal allyl carbons.[6b] Symmetrical allyllithium bridging is found in (1,3-diphenylallyl)lithium.[6c] However, this compound crystallizes as a polymer, with the lithium cations connecting the terminal carbon atoms of planar 1,3-diphenylallyl anion stacks.

In order to gain more insight into the structure of monomeric allyllithium(s), which according to all ab initio calculations are symmetrically bridged with hydrogens (substituents) bent out of the CCC plane,[7] we have now determined the X-ray structure of 1,3-bis(trimethylsilyl)allyllithium–*N,N,N′,N′*-tetramethylethylenediamine (**1**·TMEDA). This structure and model calculations[8] provide a new interpretation for Fraenkel, Chow, and Winchester's[1] dynamic NMR observations in solution.

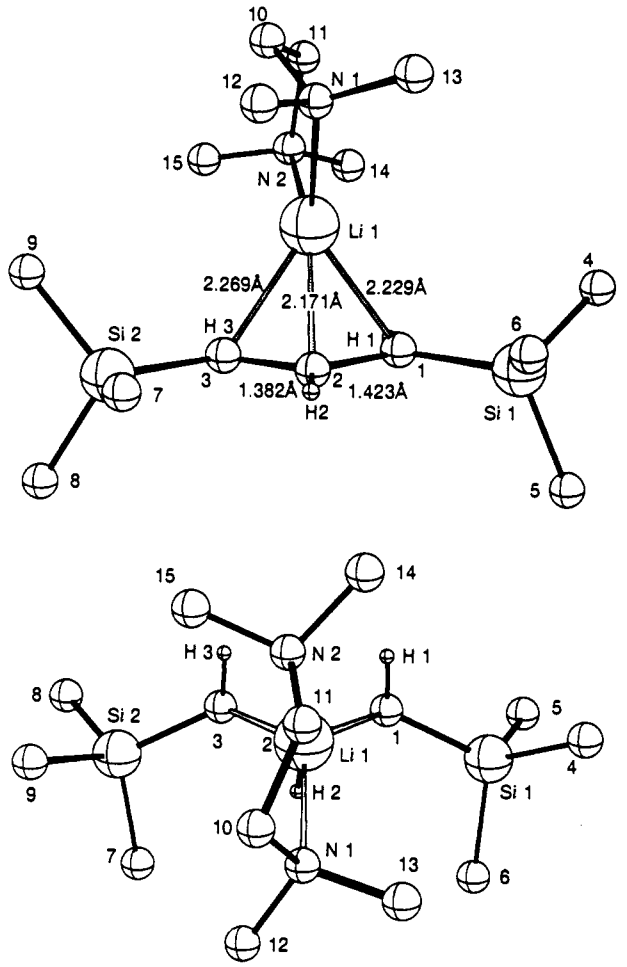


Figure 1. (a) Crystal structure of **1**·TMEDA. (b) View from the TMEDA ligand normal to the C(1)–C(2)–C(3) plane. Some important bond lengths (pm), angles (deg), and dihedral angles (deg): C(1)–C(2) = 142.3 (7); C(2)–C(3) = 138.2 (7); Li(1)–C(1) = 222.9 (9); Li(1)–C(2) = 217.0 (9); Li(1)–C(3) = 226.9 (10); Li(1)–N(1) = 207.5 (9); Li(1)–N(2) = 208.5 (9); C(1)–Si(1) = 181.5 (5); C(3)–Si(2) = 183.6 (5); C(1)–C(2)–C(3) = 129.4 (4); C(2)–C(1)–Si(1) = 125.1 (3); C(2)–C(3)–Si(2) = 125.8 (4); N(1)–C(10)–C(11)–N(2) = 57.8 (6); H(1)–C(1)–C(2)–C(3) = −11 (3); C(1)–C(2)–C(3)–H(3) = 13 (3); Si(1)–C(1)–C(2)–C(3) = 178.7 (4); C(1)–C(2)–C(3)–Si(2) = −174.8 (4); Si(1)–C(1)–C(2)–H(2) = 5 (3).

Crystal Structure of *exo,exo*-[1,3-Bis(trimethylsilyl)allyl]lithium–*N,N,N′,N′*-Tetramethylethylenediamine (1·TMEDA)

The crystal structure of monomeric **1**·TMEDA[9] is shown in Figure 1a. Figure 1b gives a view of the TMEDA ligand normal to the C(1)–C(2)–C(3) plane.

(3) We have previously observed similar dynamic NMR phenomena for *N*-lithiocarbazole in the presence of TMEDA. This species was shown to coexist as a TMEDA-solvated syn dimer/anti dimer mixture in a 1/3 molar ratio in toluene at low temperatures. At 208 K coalescence is observed for the TMEDA methyl carbon atoms, corresponding to $\Delta G^{\ddagger}$ = 10.0 ± 0.4 kcal/mol.[4] At 183 K, the CH_2 carbon atoms become nonisochronous, equivalent to $\Delta G^{\ddagger}$ = 9.4 ± 0.8 kcal/mol. Sharp NMR signals of uncomplexed TMEDA were observed over the entire temperature range (172–235 K), indicating slow exchange between free and complexed TMEDA. Gregory, K.; Bremer, M.; Bauer, W.; Schleyer, P. v. R.; Lorenzen, N. P.; Kopf, J.; Weiss, E. *Organometallics* **1990**, *9*, 1485.

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(9) **1**·TMEDA crystallizes in the monoclinic space group $C2/c$, a = 19.63 (3) Å, b = 11.788 (2) Å, c = 19.56 (2) Å, β = 101.28 (5)°, V = 4450 Å^3 at 173 K, Z = 8, d_{calcd} = 0.921 g/cm^3 for fw = 308.6. Refinement of 224 parameters using 2407 reflections with $F > 4\sigma(F)$ gave residuals R = 6.79%, wR = 7.70%. The atomic positions of H(1), H(2), and H(3) have been refined, the other H atoms using a riding model. Common isotropic temperature factors have been used for all the hydrogens. The data have been corrected with DIFABS.[10]

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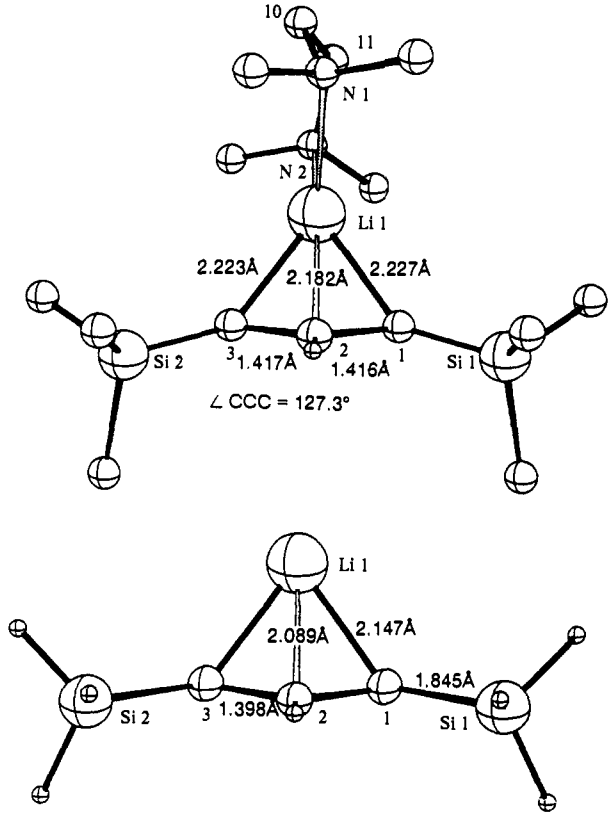

Figure 2. (a, top) MNDO calculated structure of **1**·TMEDA. (b, bottom) Ab initio (6-31G*//6-31G*) calculated structure of **1′** ($Si(CH_3)_3$ groups modeled by SiH_3).

Although hardly visible in Figure 1, Li^+ is located slightly unsymmetrically above the allyl carbon atoms: Li(1)–C(1) = 222.9 (9) pm; Li(1)–C(3) = 226.9 (10) pm. The shorter Li(1)–C(1) distance goes along with a longer C(1)–C(2) distance (142.3 (7) pm vs C(2)–C(3) = 138.2 (7) pm). As predicted by calculations,[7] **1**·TMEDA shows the bending of the hydrogens (substituents) at the allyl carbons: The inner hydrogens H(1) and H(3) are strongly bent away from lithium (H(1)–C(1)–C(2)–C(3) = −11 (3)°; C(1)–C(2)–C(3)–H(3) = 13 (3)°) while H(2) is slightly bent toward the metal (out-of-plane angle 4 (3)°). Allyllithium calculations predicted the exo hydrogens—in the case of **1**·TMEDA replaced by the trimethylsilyl groups—to be closest to the C(1)–C(2)–C(3) plane. This is at least the case for Si(1) (Si(1)–C(1)–C(2)–C(3) = 178.7 (4)°); Si(2) is more bent toward Li^+ (C(1)–C(2)–C(3)–Si(2) = −174.8 (4)°). The C(1)–C(2)–C(3) angle is strongly widened to 129.4 (4)°, again corresponding to the computational results.[7] It is reasonable to assume that the structure of the *exo,exo*-bis(trimethylsilyl)allyl anion unit of **1**·TMEDA in solution is similar to that in the crystal. Hence, the C(1)–C(2)–C(3) angle widening is shown again to be the main cause for the abnormally small $^{13}C(2)$–H(2) coupling constant (138 Hz).[7b-d,11] H(2) out-of-plane bending[12] and σ-polarization due to the π-charge have smaller influences.[7d]

The crystal structure of **1**·TMEDA also provides insight into the ^{13}C NMR shift differences between C(1) and C(3) of allyl and the $(CH_3)_2N$ groups of TMEDA in the solution investigations of **1**·TMEDA. The C_s symmetry of the *exo,exo*-bis(trimethylsilyl)allyl anion unit is disturbed by the C_2 symmetry of the twisted TMEDA ligand (N(1)–C(10)–C(11)–N(2) = 57.8 (6)°), leading to overall C_1 symmetry. The characteristics of the experimental

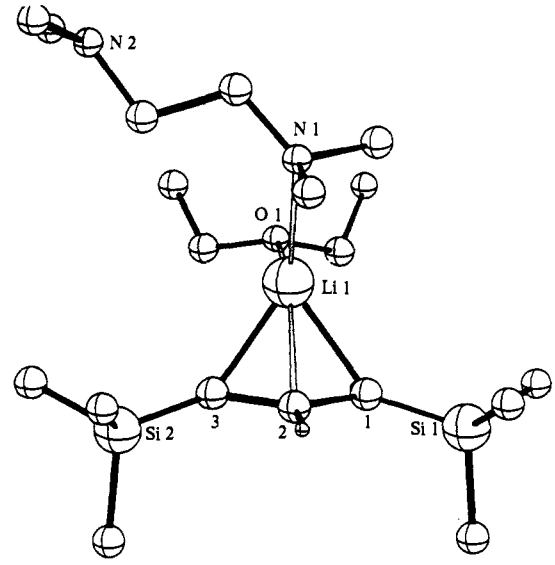

Figure 3. MNDO calculated structure of **1**·TMEDA·DEE.

structure of **1**·TMEDA are reproduced reasonably well by MNDO calculations[13] (Figure 2a): C(1)–C(2)–C(3) = 127.3°, N(1)–C(10)–C(11)–N(2) = 49.9°.

Without TMEDA, structures with C_s symmetry are obtained both in MNDO and 6-31G*//6-31G* ab initio calculations (**1′** (Figure 2b), the $(H_3C)_3Si$ groups were modeled by H_3Si).

Dynamics of 1·TMEDA in Diethyl-d_{10} Ether Solution

A consequence of the C_1 symmetry is that C(1) and C(3) will be chemically nonequivalent. (As discussed below, the same is true for all four methyl groups of the TMEDA ligand.) An IGLO calculation,[14] using a double-ζ basis set,[15] on the experimental structure of the allyl moiety gives a chemical shift difference of almost 12 ppm![16] Thus, additional complexation of the lithium cation in **1** by a molecule of diethyl ether, proposed to account for the chemical nonequivalence of C(1) and C(3),[1] now appears to be unnecessary. We tried to calculate the structure of such a complex with formally hexacoordinate lithium, but one of the lithium–nitrogen bonds cleaves upon MNDO optimization. The lithium cation in the resulting structure is pentacoordinate (Figure 3).

What is the mechanism for the observed coalescence of C(1) and C(3) as well as of all the methyl carbons of the TMEDA ligand? Fraenkel, Chow, and Winchester found similar activation energies for the dynamic processes leading to both kinds of signal averaging and concluded that the same process is involved.[1] We explain the observed dynamic processes on the basis of two motions within the complex **1**·TMEDA: (1) rotation of the Li^+–TMEDA moiety with respect to the allyl anion, which results in coalescence of C(12) and C(14) as well as C(13) and C(15), and (2) twisting of the TMEDA ligand (i.e., inversion of the N–C–C–N dihedral angle), which leads to coalescence of C(12) and C(13), C(14) with C(15), and C(1) with C(3).

The MNDO-calculated barriers are 9.3 kcal/mol for motion 1 but only 2.9 kcal/mol for motion 2. The latter is much lower than the experimental value. However, this is due to the known deficiencies of MNDO, e.g., that nonbonded repulsions are overestimated.[17] Thus, puckered rings are calculated to be too flat, and inversion barriers are too low. Hence, MNDO is expected

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(16) This value clearly is exaggerated, due to the absence of the silyl groups which were replaced by hydrogens in the IGLO calculation.

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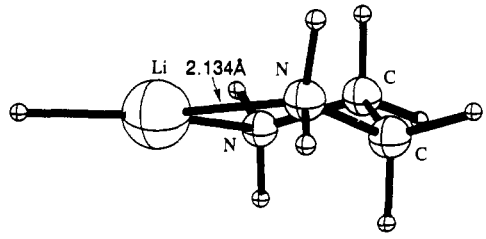

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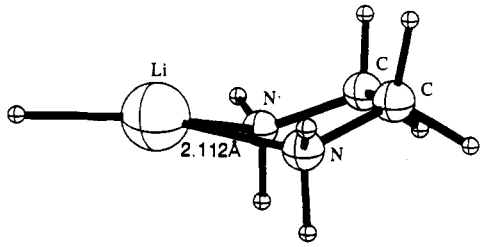

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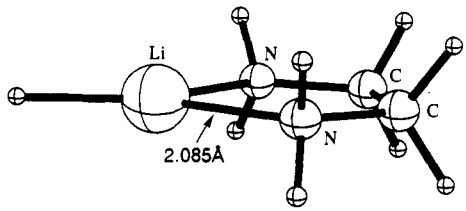

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Figure 4. Ab initio (6-31+G*//6-31+G*) calculated structures of complex **2** of lithium hydride and ethylenediamine and two possible transition structures, **3** and **4**, for ring inversion.

to underestimate the inversion barrier for the LiNCCN five-membered ring (motion 2). This is shown by a calibration of the MNDO results for a model system, the complex of lithium hydride and ethylenediamine, with ab initio computations. The structures of this complex **2** and of two possible transition structures for ring inversion, **3** and **4**, are shown in Figure 4.

The most stable structure **2** has C_2 symmetry (frequency analysis shows this to be a true minimum both at MNDO and 6-31+G*). This conformation is found in numerous X-ray crystal structures.[18] The transition structure **3** for ring inversion has C_s symmetry, with only the methylene hydrogens eclipsed. The activation barrier, at MP2/6-31+G*//6-31+G*, corrected for differences in zero-point vibrational energy, is 6.9 kcal/mol, in contrast to the much lower MNDO barrier of 2.4 kcal/mol. The C_{2v} structure **4**, with all hydrogens eclipsed, is a saddle point of order 2. At MP2/6-31+G*//6-31+G* + ΔZPE, this structure is 8.0 kcal/mol less stable than the C_2 minimum (MNDO gives a value of only +3.4 kcal/mol).

The influence of the amine methyl groups in TMEDA on the ring inversion barrier should be negligible. With MNDO, a barrier of 2.2 kcal/mol was calculated for inversion of the HLi-TMEDA complex, as compared to 2.4 kcal/mol for HLi-EDA.

An alternative coalescence process has been proposed.[3] If one of the nitrogen-lithium bonds were broken, the resulting monocoordinating TMEDA would become much more flexible.

(18) See Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

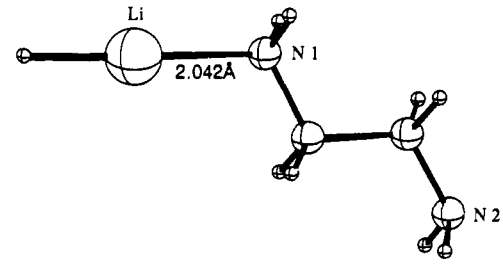

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Figure 5. Ab initio (6-31+G*//6-31+G*) calculated structure of the monodentate complex **5** of lithium hydride and ethylenediamine.

Recombination would result in the equivalence observed by NMR. We evaluated this process for the HLi-EDA model with only one nitrogen of the ethylenediamine ligand bound to lithium hydride (**5**, Figure 5).

At MP2/6-31+G*//6-31+G* + ΔZPE, this monodentate complex **5** is 11.8 kcal/mol higher in energy than the most stable C_2 complex **2** with both nitrogens coordinated to lithium. Note that this would imply a barrier ca. 5 kcal/mol higher in energy than that corresponding to transition structure **3**. The solvent, diethyl ether, might compensate for the breaking of one of the coordinative N-Li bonds, but exchange with a second, free TMEDA would be expected to occur as well. This is not observed experimentally. Hence, we do not favor this one-process model.

If TMEDA does not become partially disattached, two motions are necessary to explain the experimental results. The calculated barriers, (1) rotation of Li^+-TMEDA (9.3 kcal/mol; MNDO) and (2) twisting of TMEDA (6.9 kcal/mol; MP2/6-31+G*//6-31+G* + ΔZPE), nicely agree with the experimental $\Delta H^{\ddagger}$ = 7.7 kcal/mol. We suggest that the dynamics observed in the low-temperature NMR investigations of **1**·TMEDA in diethyl-d_{10} ether correspond to a composite of both these motions, which fortuitously have nearly the same barriers.

Conclusions

While allyl anions are inherently symmetrical species, small deviations in geometry can result from ligand interaction with the counterion. This resulting symmetry reduction, e.g., as found in the X-ray structure of **1**·TMEDA, can also be observed in solution from NMR measurements. The dynamic NMR observations reported earlier, i.e., coalescence of C(1) and C(3) and of the TMEDA methyl groups, are now explained by two processes, rotation of the Li^+-TMEDA with respect to the 1,3-bis(trimethylsilyl)allyl anion and inversion of the Li^+-TMEDA five-membered ring. MNDO and ab initio calculations show both these processes to have nearly the same activation energy.

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Supplementary Material Available: Tables of the structure determination summary, atomic positional parameters and isotropic equivalent temperature parameters, bond lengths, bond angles, anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters, and calculated geometries, in the form of "archive entries" (9 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.