A Crystallographic and Computational Study of a Diethyl Ether Complex of Fluorenyllithium

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Received May 30, 1997

The structure of a diethyl ether (DEE) complex of fluorenyllithium, [Li($C_{13}H_9$)($DEE)_2$], was investigated by X-ray crystallography and quantum chemical calculations. In the crystal structure, the lithium cation interacts in an η^2-arrangement with the fluorenyl anion at distances of 2.26 and 2.31 Å away from C9 and C10. In contrast to the uncomplexed ion pair where recent calculations revealed that Li^+ is situated over the five-membered ring, calculations at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level show that for the DEE-coordinated complex, the optimal structure resembles the X-ray structure. Since the η^2-arrangement is the global minimum in both the solid state and gas phase, it was concluded that crystal packing is not the main factor that causes the lithium cation to change position when going from the uncomplexed to the DEE-complexed fluorenyllithium. A comparison with the smaller water-coordinated complex indicates that intramolecular steric interactions within the DEE-coordinated complex lead to an η^2-arrangement instead.

Introduction

The structure and reactivity of organolithium compounds are of fundamental interest since they are widely used as reagents in organic and organometallic synthesis. Accordingly, the structures of a great number of organolithium compounds have been studied in solution by different spectroscopic methods, mainly NMR spectroscopy,[1] and in the solid state by X-ray crystallography.[2] Organolithium compounds are often present as different types of ion pairs or aggregates both in solution and in the solid state. It is known that the degree of aggregation and solvation influences the reactivity and stereoselectivity in reactions.[3]

In an ongoing project, solid-state NMR spectroscopy is used to relate X-ray and NMR data sources and to check whether solid-state structures of organolithium compounds as determined by X-ray crystallography are relevant models for structures in solution.[4]

To do this, we studied various fluorenyllithium complexes by solid-state ^{13}C NMR spectroscopy.[4a] The reason for this choice of complexes was that the ion pair situation of the fluorenyllithium system in solution has been thoroughly investigated by absorption[5] and NMR spectroscopy.[6] A number of X-ray studies of fluorenyllithium derivatives have also been reported.[7] Of most relevance to the present discussion is the quinuclidine complex,[7a] as it represents a contact ion pair (CIP), and the THF solvent-separated ion pair (SSIP) of

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(1) (a) Günther, H.; Moskau, D.; Bast, P.; Schmalz, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1212. (b) Thomas, R. D. *Isotopes in the Physical and Biomedical Science*; Buncel, E., Jones, J. R., Eds.; Elsevier: Amsterdam, 1991. (c) Bauer, W.; Schleyer, P. v. R. *Adv. Carbanion Chem.* **1992**, *1*, 89. (d) Bauer, W. *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience Publications: New York, 1995.

(2) (a) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (c) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (d) Boche, G.; Lohrenz, J. C. W.; Opel, A. *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience Publications: New York, 1995. (e) Pauer, F.; Power, P. *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience Publications: New York, 1995.

(3) (a) Juaristi, E.; Beck, A. K.; Hansen, J.; Matt, T.; Mukhopadhyay, T.; Simson, M.; Seebach, D. *Synthesis* **1993**, *12*, 1271. (b) Jackman, L. M.; Petrei M. M.; Smith, B. D. *J. Am. Chem. Soc.* **1991**, *113*, 3451. (c) Schlosser, M., Guest Ed. *Tetrahedron* **1994**, *50* (20), 5845. (d) Beak, P.; Basu, A.; Gallagher, D. J.; Park, Y. S.; Thayumanvan, S. *Acc. Chem. Res.* **1996**, *29*, 552.

(4) (a) Johnels, D.; Edlund, U. *J. Am. Chem. Soc.* **1990**, *112*, 1647. (b) Johnels, D.; Edlund, U. *J. Organomet. Chem.* **1990**, *393*, C35. (c) Johnels, D. *J. Organomet. Chem.* **1993**, *445*, 1. (d) Johnels, D.; Andersson, A.; Boman, A.; Edlund, U. *Magn. Reson. Chem.* **1996**, *34*, 908. (e) Quist, P.-O.; Förster, H.; Johnels, D. *J. Am. Chem. Soc.* **1997**, *119*, 5390.

(5) (a) Smid, J. *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972. (b) Vos, H. W.; MacLean, C.; Velthorst, N. H. *J. Chem. Soc.* **1976**, *72*, 63.

(6) (a) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661. (b) O'Brien, D. H.; Russel, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (c) Hoffman, D.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 208. (d) Sethson, I.; Eliasson, B.; Edlund, U. *Magn. Reson. Chem.* **1991**, *29*, 1012.

(7) (a) Brooks, J. J.; Rhine W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339. (b) Walczak, M.; Stucky, G. D. *J. Organomet. Chem.* **1975**, *97*, 313. (c) Bladauski, D.; Rewicki, D. *Chem. Ber.* **1977**, *110*, 3920. (d) Schmidt, H.-J.; Rewicki, D. *Acta Crystallogr.* **1984**, *A40*, C293. (e) Buchholtz, S.; Harms, K.; Marsch, M.; Massa, W.; Boche, G. *Angew. Chem.* **1989**, *101*, 57. (f) Becker, B.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **1989**, *101*, 501. (g) Culp, R. D.; Cowley, A. H. *Organometallics* **1996**, *15*, 5380. (h) Hoffmann, D.; Schleyer, P. v. R.; Stalke, D. Unpublished work. (i) Diaz, H. V. R.; Wang, Z.; Bott, S. G. *J. Organomet. Chem.* **1996**, *508*, 91. (j) Könemann, M.; Erker, G.; Fröhlich, R.; Würtwein, E.-U. *J. Am. Chem. Soc.* **1997**, *119*, 11155. (k) Håkansson, M.; Norberg, S.; Swahn, M.; Werner, L. Unpublished work.

S0276-7333(97)00450-0 CCC: $15.00
Publication on Web 02/27/1998

fluorenyllithium[7h,k] and 1,ω-bis(9-lithiofluoren-9-yl)ethane and -hexane.[7f] After the submission of this paper, a structure determination of another DEE complex of fluorenyllithium was reported.[7j] This complex was obtained as an impurity in the synthesis of an aminofulvene. In contrast to the complex presented in this paper, only one DEE is interacting with the lithium cation, producing a stacking of the fluorenyl units into a polymeric chain. Recently, some further CIP fluorenyllithium complexes were reported where a nitrogen-containing pendant arm at the 9-position occupies one of the ligation sites on lithium.[7g,i] Depending on the neutral ligand used in each of these systems, either an η^2 or η^5 interaction between lithium and the fluorenyl anion was formed.[7g] If no complexing agent is present, a sandwich structure is observed,[7d] while if a protic complexing agent is used, hydrogen-bonded structures can be formed.[7e]

The results from our ^{13}C solid-state NMR studies show that the structure of the complexes is dependent on the type of neutral ligand used.[4a] In the quinuclidine complex, the lithium cation was found to be unsymmetrically positioned relative to the fluorenyl framework, in accordance with the earlier reported X-ray structure.[7a] This is also true for the diethyl ether (DEE) complex. However, in the *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) complex, the system is claimed to be symmetric, as determined by ^{13}C solid-state NMR spectroscopy. Similarly, the THF-coordinated system shows a symmetric structure.[4a]

The same conclusions were obtained from ^{7}Li solid-state NMR studies, where the chemical shift was determined under MAS conditions and the quadrupolar interaction of the lithium cation was studied under static conditions.[4d] According to these results, the lithium cation is situated above the central five-membered ring in the TMEDA complex. This was later confirmed by a REDOR study of this complex.[4e] The NMR data of the THF complex indicate an SSIP structure even in the solid state, i.e., in accordance with recent X-ray studies of this system.[7h,k] The exact structure of the DEE complex of fluorenyllithium could not be deduced from the NMR data. It is known from the ^{13}C NMR study that the lithium cation is located asymmetrically relative to the carbon framework. From the ^{7}Li NMR chemical shift, it is clear that the lithium cation still experiences the ring current of the aromatic system but not to the same extent as in the TMEDA complex. The quadrupolar coupling constant is relatively high, but not as high as in the quinuclidine complex (188 vs 262 kHz, respectively).

In this paper, we report an X-ray crystallographic study, as well as a quantum chemical investigation, of a DEE complex of fluorenyllithium.

Results and Discussion

The solid-state NMR investigations support the view that the actual hapticity and position of the lithium cation in the fluorenyllithium complexes depend on the neutral ligand used.[4a,d,7g]

A related system that has been thoroughly investigated is complexes of benzyllithium. Several X-ray crystallographic studies have been reported,[8] where the lithium location relative to the carbanion also varies depending on the ligands used. The 1,4-diazabicyclo[2.2.2]octane (DABCO) structure is similar in structure to the quinuclidine complex of fluorenyllithium, i.e., an alleged η^3 structure, except that both nitrogens are involved in interactions with the lithium cations in the DABCO ligand, thereby producing a polymer.[8a] It is interesting to note that this ligand has steric requirements that are very similar to those of quinuclidine. Other types of structures containing an η^1 interaction with the C_α carbon in the TMEDA/THF complex have also been observed.[8c] In the TMEDA complex of trimethylsilyl-substituted benzyllithium, an η^2 structure was observed.[8d] In the other complexes, polymers form where two lithium cations interact in a distorted η^2 mode with C_α and the ipso-carbon.[8b,e]

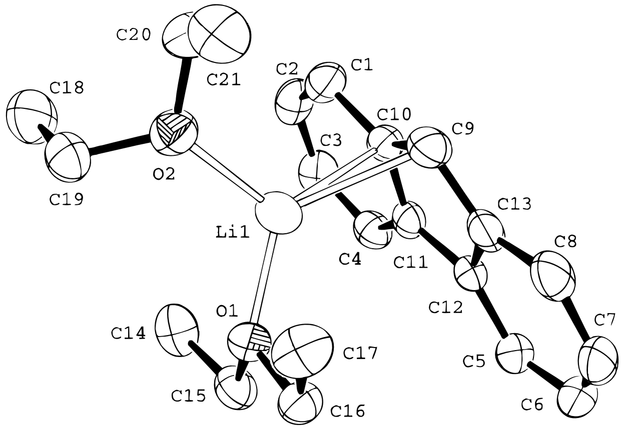

Figure 1. ORTEP drawing of the DEE complex of fluorenyllithium (**1**) showing the crystallographic numbering.

The general conclusion from these investigations is that the potential-energy surface above a delocalized carbanionic system is relatively shallow and that the actual minimum energy structure of a given complex may be determined by the steric requirements of the ligands and/or by crystal packing effects.

Crystal Structure of the DEE Complex of Fluorenyllithium, [Li($C_{13}H_9$)(DEE)$_2$] (1). The molecular structure and the crystallographic numbering of **1** is shown in Figure 1. Crystal and experimental data are summarized in Table 1, and selected interatomic distances and angles are given in Table 2. The lithium atom can be considered to be three-coordinate with two ether oxygens and the midpoint of the C9−C10 bond, which creates a trigonal-planar coordination with lithium in the trigonal plane, within experimental errors. Another interpretation is that fluorenyl acts as an η^2 ligand, resulting in a distorted tetrahedral environment around lithium with an acute C1−Li1−C10 angle of 36°. The O1−Li1−O2 angle of 115° lies between a trigonal-planar and a tetrahedral geometry. Similar η^2 coordination geometries in organolithium chemistry have been observed, e.g., in the bis-quinuclidine complex of

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(8) (a) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150. (b) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117. (c) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 2303. (d) Zarges, W.; Marsch, M.; Harms, K.; Koch, W.; Frenking, G.; Boche, G. *Chem. Ber.* **1991**, *124*, 543. (e) Muller, G.; Lutz, M.; Waldkricher, M. *Acta Crystallogr.* **1996**, *C52*, 1182.

Table 1. Crystallographic Data for $[Li(C_{13}H_9)(DEE)_2]$ (1)

formula	$C_{21}H_{29}LiO_2$
fw	320.4
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	7.654(7)
b, Å	13.878(5)
c, Å	18.407(4)
β, deg	97.13(4)
V, Å^3	1940(2)
Z	4
d_{calc}, g/cm^3	1.10
F(000)	696
cryst dimens mm	0.20 × 0.20 × 0.20
radiation	Mo Kα (0.710 73 Å)
μ, mm^{-1}	0.067
T, °C	−110
data collected, deg	$5.0 < 2\theta < 50.0$
index ranges	$0 \leq h \leq 9, 0 \leq k \leq 16, -21 \leq l \leq 21$
abs corr	ψ-scans
transm coeff	0.97−1.00
total no.of reflns	3692
no. unique reflns	3419 [R(int) = 0.0611]
no. params	333
final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0404$, w$R_2 = 0.110$
max residual electron density, e/Å^3	0.16
min residual electron density, e/Å^3	−0.19

Table 2. Selected Intramolecular Distances (Å) and Angles (°) for 1

Li(1)−O(1)	1.894(6)	C(4)−C(11)	1.409(4)
Li(1)−O(2)	1.909(6)	C(5)−C(6)	1.387(5)
Li(1)−C(9)	2.256(7)	C(5)−C(12)	1.404(4)
Li(1)−C(10)	2.306(7)	C(6)−C(7)	1.385(6)
Li(1)−C(1)	2.915(8)	C(7)−C(8)	1.374(5)
Li(1)−C(11)	2.868(8)	C(8)−C(13)	1.422(4)
Li(1)−C(12)	3.159(8)	C(9)−C(10)	1.424(4)
Li(1)−C(13)	2.825(8)	C(9)−C(13)	1.426(5)
C(1)−C(2)	1.381(5)	C(10)−C(11)	1.443(4)
C(1)−C(10)	1.420(4)	C(11)−C(12)	1.434(4)
C(2)−C(3)	1.396(5)	C(12)−C(13)	1.443(5)
C(3)−C(4)	1.376(5)		
O(1)−Li(1)−O(2)	114.6(3)	C(1)−C(10)−C(9)	132.6(3)
O(1)−Li(1)−C(9)	126.7(3)	C(1)−C(10)−C(11)	118.3(3)
O(2)−Li(1)−C(9)	114.7(3)	C(9)−C(10)−C(11)	109.1(3)
O(1)−Li(1)−C(10)	126.7(3)	C(4)−C(11)−C(12)	132.5(3)
O(2)−Li(1)−C(10)	115.4(3)	C(4)−C(11)−C(10)	120.1(3)
C(9)−Li(1)−C(10)	36.36(14)	C(12)−C(11)−C(10)	107.3(3)
C(2)−C(1)−C(10)	119.7(3)	C(5)−C(12)−C(11)	132.3(3)
C(3)−C(4)−C(11)	119.6(3)	C(8)−C(13)−C(9)	132.8(3)
C(6)−C(5)−C(12)	119.1(4)	C(9)−C(13)−C(12)	109.0(3)
C(10)−C(9)−C(13)	107.2(3)		

fluorenyllithium,[7a] ferrocenophanyllithium,[9] and in some of the benzyllithium complexes mentioned.[8a,d,e]

An important difference in the present complex (**1**) from the earlier reported quinuclidine complex of fluorenyllithium[7a] is the position of the lithium atom with respect to the fluorenyl ligand. From Figure 2, it can be seen that in **1** Li1 is positioned straight above C9 and C10, which can be expressed as a centroid (C9,-C10,C11,C12,C13)−midpoint(C9−C10)-Li1 angle of 92.1°, while in fluorenyllithium bis-quinuclidine[7a] the projection of lithium onto the fluorenyl plane sets the lithium atom more than 1 Å away from the closest point of the anion. On the other hand, the projection of Li1 onto the mean plane of the five-membered ring of the fluorenyl ligand in **1** is similar to that found in {9-[2-(dimethylamino)ethyl]fluorenyl}Li(THF)$_2$.[7g]

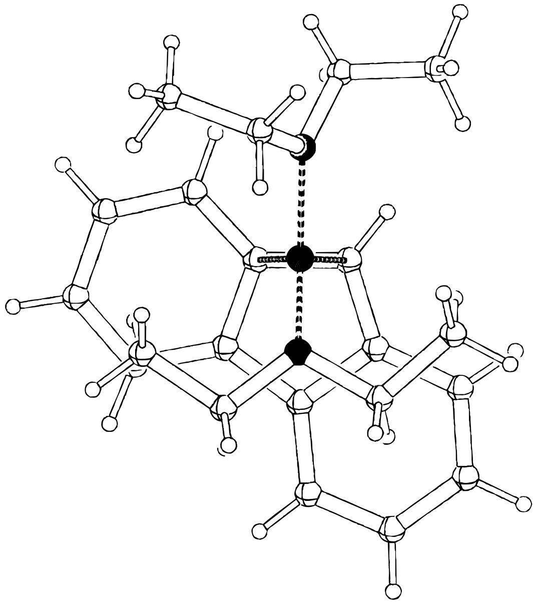

Figure 2. Alternative view of **1** showing the lithium cation positioned over the C9−C10 bond and the arrangement of the DEE ligands relative to the fluorenyl framework.

The average Li−O distance in **1** of 1.90 Å is close to a normal lithium−ether interaction and is significantly shorter than the average Li−N distance of 2.03 Å in fluorenyllithium bis-quinuclidine. More interestingly, the average Li−C distance of 2.28 Å is shorter than in fluorenyllithium bis-quinuclidine, where the Li−C average distance is 2.40 Å. In {9-[2-(dimethylamino)ethyl]-fluorenyl}Li(THF)$_2$,[7g] which also is η^2, the Li−C average distance is 2.52 Å. Both η^3 and η^5-fluorenyl complexes have significantly larger Li−C average distances than that of 2.28 Å found in **1**.[7] The average literature value for aryl carbons bonded to lithium is 2.29 Å.[2a] In fluorenyllithium bis-quinuclidine, the fluorenyl anion departs from planarity in such a way that the equivalent of C9 in **1** is displaced 0.04 Å away from the best plane of a benzyl fragment toward lithium. In **1**, this deviation of C9 from the C1−C2−C3−C4−C11−C10 plane is 0.10 Å, which is in the same range as in benzyllithium triethylenediamine.[3a] The shorter Li−C bond lengths together with this larger deviation of C9 from planarity in the present complex would seem to indicate a stronger lithium interaction with the fluorenyl anion in **1** as compared to the fluorenyllithium bis-quinuclidine complex.

Figure 2 also shows the symmetrical positioning of the O1 diethyl ether ligand with respect to the fluorenyl anion. In this context, it is important to note that interatomic contacts are of the same magnitude as the intra-atomic ether−fluorenyl contacts, which is visualized in the unit cell packing stereogram in Figure 3. Both intra and inter H···H contacts lie in the 2.3−2.4 Å range, and also the shortest intramolecular fluorenyl/carbon C···H contacts (e.g., C4···H14A = 2.75 Å) are comparable to the shortest intermolecular contacts (e.g., C10···H16B = 2.73 Å). Crystal packing effects, thus, can not be disregarded when considering molecular conformations in the solid.

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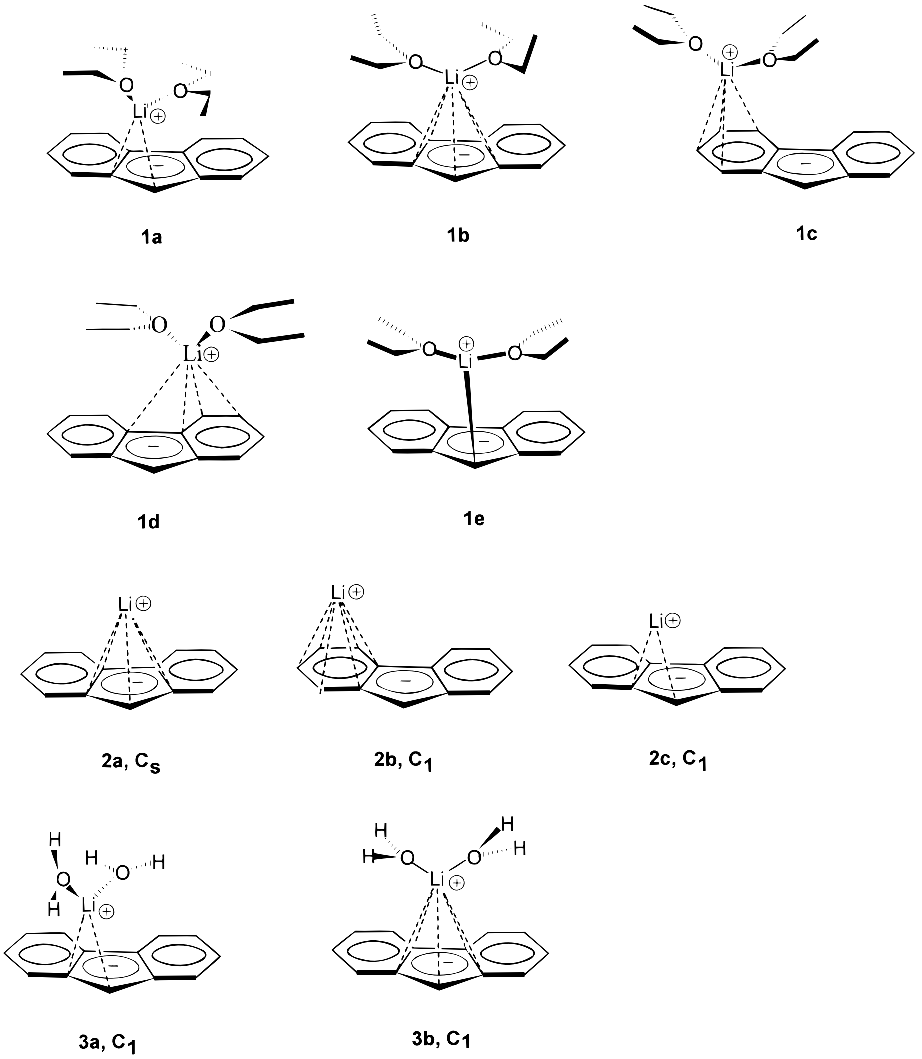
(9) Ahlberg, P.; Davidsson, Ö.; Hilmersson, G.; Löwendahl, M.; Håkansson, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1573.

Scheme 1



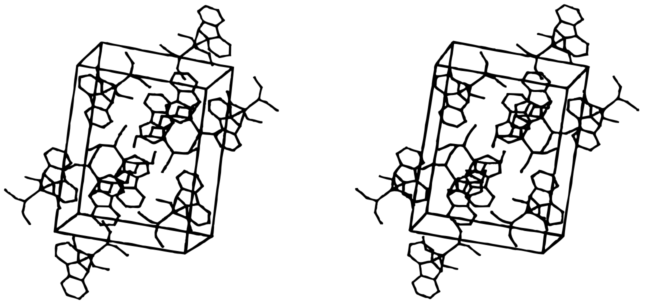


Figure 3. Unit cell packing stereogram of **1**.

Computational Investigation. The question is whether the complex has $Li^+(DEE)_2$ centered over the five-membered ring in an η^5-arrangement in the gas phase and that crystal packing effects force the complex into the η^2-structure found in the solid, or if intramolecular factors favor this arrangement so that it also corresponds to the global minimum in the gas phase. To clarify this, quantum chemical calculations were carried out.

There are already a few theoretical studies reported on fluorenyllithium.[7j,10] In these studies, the global minimum was found when the lithium cation is located above the five-membered ring (**2a**, Scheme 1) but local minima were also found when Li^+ is situated over the six-membered ring (**2b**) or interacting with C9 and C10 (**2c**), similar to the bis-quinuclidine complex. In the most recent study by Schleyer and co-workers,[10d] **2a** was calculated to be 4.6 kcal/mol more stable than **2b** at the B3LYP/6-311+G(d)//B3LYP/6-31G(d) + ZPE level. In addition, **2c** was found to be 5.9 kcal/mol above **2a** at the MNDO level.[10a] We investigated whether there is also a minimum that resembles **2c** at the HF/6-31G(d) and B3LYP/6-31G(d) levels, however, in contrast to the MNDO calculations,[10a] no minimum corresponding to such a structure could be found.

As previously proposed, the potential-energy surface above delocalized anionic systems such as the fluorenyl anion is rather flat,[10b,c] and therefore, steric and crystal packing effects could have a considerable impact on the overall solid-state structure of aggregates containing delocalized anions. Nevertheless, previous computational work suggests that covalency plays a nonnegligible role for the structure of benzyllithium,[11] and if

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[10] (a) Lipkowitz, K. B.; Uhegbu, C.; Naylor, A. M.; Vance, R. *J. Comput. Chem.* **1985**, *6*, 662. (b) Bushby, R. J.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 265. (c) Bushby, R. J.; Steel, H. L.; Tytko, P. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1155. (d) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAlister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075.

[11] Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 821.

Table 3. Selected Geometrical Data for the Minimum Structure of 1 at Various Computational Levels[a]

	PM3 (**1e**)	MNDO (**1a**)	HF/6-31G(d) (**1a**)	B3LYP/6-31G(d) (**1a**)
Li−C9	2.136	2.046	2.207	2.173
Li−C10	2.873	2.372	2.405	2.338
Li−C11	3.834	3.453	2.938	2.860
Li−C12	3.911	3.811	3.126	3.045
Li−C13	3.037	3.141	2.750	2.686
Li−C1	3.465	2.768	3.113	3.071
Li−C8	3.763	4.119	3.702	3.656
Li−O1	2.037	2.242	2.008	1.985
Li−O2	2.000	2.256	1.993	1.953
C9−Li−O1	128.0	122.7	132.9	133.6
C9−Li−O2	119.9	123.0	115.9	116.0
O1−Li−O2	111.8	113.3	108.1	107.3
Li−C9−C10	104.4	82.8	79.7	77.9
Li−C9−C13	113.8	126.0	95.9	94.1
hapticity	η^1	η^2	η^2	η^2

[a] Bond distances are given in angstroms and angles are given in degrees.

so, this could also influence the structure of fluorenyllithium complexes.

According to Stucky, possible conformations of Li($C_{13}H_9$)(DEE)$_2$ can be derived by considering orbital interactions between the HOMO of the fluorenyl anion and the 2pπ(Li^+) acceptor orbital of the cationic Li(DEE)$_2^+$ fragment.[7a] Such interactions would lead to the possible structures **1a**−**d** in Scheme 1. However, if the interaction is electrostatic,[12] Li(DEE)$_2^+$ would interact with the most negatively charged site, C9, of the fluorenyl anion, leading to the η^1-arrangement **1e**.

The structures **1a**−**e** were first analyzed at the semiempirical MNDO and PM3 levels and subsequently at the HF and B3LYP levels. Selected structural data from the calculations are reported in Table 3. With MNDO, no clear preference for any of the structures **1a**−**c** was found since the relative energies are 0.1 (**1a**), 0.0 (**1b**), and 0.6 (**1c**) kcal/mol. Structures corresponding to **1d** and **1e** were not minima according to MNDO. However, at the PM3 level, the η^1-structure **1e** is the global energy minimum. It should be noted that no stable structure which resembles **1a** could be found at this level of theory, even though a ring-centered **1b** is a local minimum 8.8 kcal/mol higher in energy than **1e**. In a recent theoretical study of lithium enolate aggregates, it was found that PM3 calculations generally give rise to reasonable geometries relative to ab initio methods.[13] The conclusion from this study was that "PM3 energies are clearly inadequate but geometries are well described by this semiempirical method".[13] However, when it comes to the more delocalized fluorenyllithium system, the global minimum is not in accordance with calculations at higher levels, vide infra.

At both the HF/6-31G(d) and B3LYP/6-31G(d) levels, the global minimum of the Li($C_{13}H_9$)(DEE)$_2$ complex is **1a**, which resembles the X-ray structure. The second most stable structure is **1b**, being less stable than **1a** by 1.9 kcal/mol at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level. A further local minimum on the potential-energy surface of Li($C_{13}H_9$)(DEE)$_2$ is **1c**. However, this geometry is less stable than **1a** by 7.4 kcal/mol at the HF/6-31G(d) level and was not further considered. The structure **1d**, with Li(DEE)$_2^+$ interacting with C5 and C12, was not found to be a minimum. Finally, in contrast to PM3 calculations, the η^1-structure **1e** is not stable at either the HF or B3LYP levels. Furthermore, preliminary calculations at the HF/3-21G level indicate that the arrangement of the DEE ligands found in the X-ray structure of **1a** is the most stable arrangement, even though the energy difference to the next stable conformation is merely 0.3 kcal/mol. Hence, since **1a** is also the global minimum in the gas phase, the HF and B3LYP calculations indicate that crystal packing is not the major effect that forces the complex away from a ring-centered η^5-structure to an η^2-structure with Li(DEE)$_2^+$ positioned over the C9−C10 bond.

At the B3LYP/6-31G(d) level, the Li−C9 and Li−C10 distances are 2.173 and 2.338 Å (Table 3), respectively. This is slightly different from the X-ray structure where the two Li−C distances are more similar (2.256 and 2.306 Å, Table 2). A somewhat larger deviation between the calculated and measured distances can be observed for the Li−O bonds. However, the overall difference in the geometry between the optimal gas-phase and solid-state structure is small and shows that intermolecular crystal packing distorts the complex from the optimal gas-phase geometry to a minor extent.

To evaluate the importance of intramolecular steric effects in Li($C_{13}H_9$)(DEE)$_2$, we also investigated the smaller complex Li($C_{13}H_9$)(H_2O)$_2$ (**3**) where steric repulsion between the fluorenyl framework and the ligands is considerably smaller. In **3**, a clear preference for coordination to the center of the five-membered ring (**3b**) was found. An attempt to locate Li(OH_2)$_2^+$ in a similar position as in the global minimum of Li($C_{13}H_9$)(DEE)$_2$ (**3a**) failed. When the Li($C_{13}H_9$)(O)$_2$ framework of **3** is frozen as in the B3LYP/6-31G(d) geometries of **1a** or **1b** (**3a′** and **3b′**, respectively) and only the positions of the H atoms of the H_2O ligands were optimized, then **3a′** is less stable than **3b′** by 2.9 kcal/mol at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level. The reversed stability ordering as compared to **1a** and **1b** is remarkable and indicates that intramolecular steric effects are important for the structure and stability of various conformations of solvated fluorenyllithium complexes. This finding also reveals that usage of H_2O to simulate etheral solvents is not appropriate in the case of organolithium complexes.[13]

From a comparison of the B3LYP/6-31G(d) geometries of **1a** and **1b**, an understanding of the magnitude of steric strain between the DEE ligands and the fluorenyl framework can be obtained. In **1b**, the O−Li−O angle is 96.9°, which is smaller than in **1a** where it is 107.3° (Table 3, Figure 4). The Li−O distances in **1b** are also longer (2.002 and 2.023 Å) than those in **1a** (1.953 and 1.985 Å). This indicates that the steric strain in **1b** elongates the Li−O distances and reduces the O−Li−O angle. However, this could also be a general difference in the geometries between ring-centered and C9−C10 bond-coordinated Li($C_{13}H_9$)(S)$_2$ complexes (S = ligand). To differentiate between these two alternatives, we analyzed the B3LYP/6-31G(d) geometry of the ring-

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(12) (a) Sannagrahi, A. B.; Kar, T.; Guha, B.; Niyogi, B.; Hobza, P.; Schleyer, P. v. R. *Chem. Rev.* **1990**, *90*, 1061. (b) Kaufmann, E.; Raghavachari, K.; Reed, A. L.; Schleyer P. v. R. *Organometallics* **1988**, *7*, 1597.

(13) Abbotto, A.; Streitwieser, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 11255.

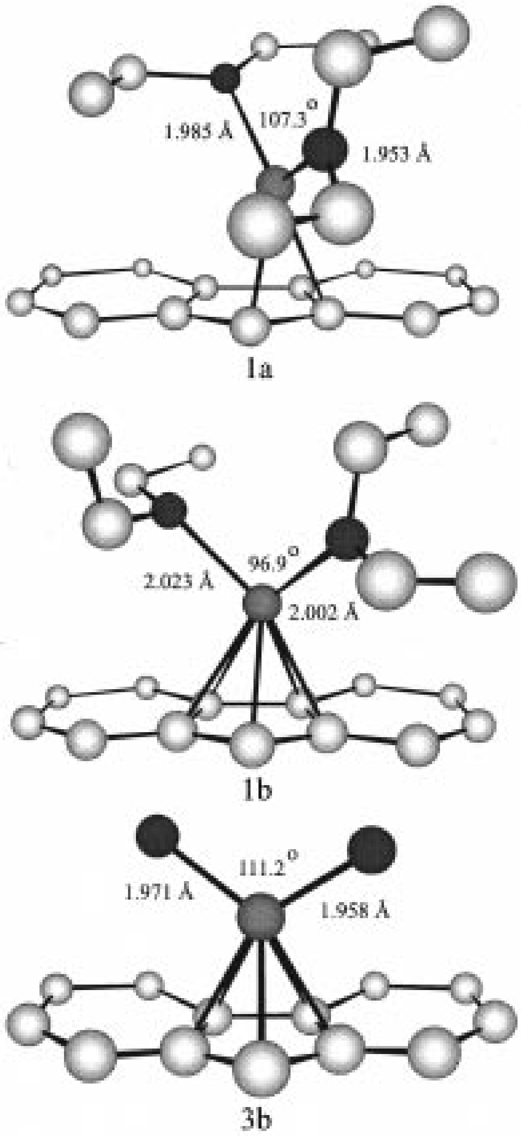

Figure 4. Selected structural parameters of the Li(DEE)$_2^+$ unit at the B3LYP/6-31G(d) level of **1a**, **1b**, and **3b**. Protons are omitted for clarity.

centered structure **3b** (Figure 4). As a result, it is found that the Li−O bond distances (1.958 and 1.971 Å) and the O−Li−O angle (111.2°) are more in agreement with the corresponding geometrical parameters in **1a** than with those in **1b**. Furthermore, the coordination energy is considerably lower in **1b** than in **3b** (92.2 vs 111.9 kcal/mol at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level). A comparison of ring-centered **1b** and **3b** also reveals that the average Li−C distance is longer in **1b** than in **3b** (2.403 vs 2.347 Å, respectively), indicating that intramolecular steric strain pushes the DEE ligands away from the fluorenyl framework and thereby lowers the stability of **1b**.

To estimate how much the geometrical distortion of the Li(DEE)$_2^+$ unit destabilizes the complex, we carried out B3LYP/6-31G(d) calculations on frozen Li(DEE)$_2^+$ as in **1a** and **1b**. An energy difference of 5.6 kcal/mol was found with the arrangement of the Li(DEE)$_2^+$ unit as in **1a** being the most stable. Since the interaction between Li(DEE)$_2^+$ and the fluorenyl anion is mainly electrostatic, steric repulsion between the DEE ligands and the fluorenyl anion makes Li(DEE)$_2^+$ adopt a less stable structure in **1b**. Thus, we conclude that intramolecular steric strain is the most important factor that determines that the DEE-solvated complex of fluorenyllithium has an η^2- rather than an η^5-structure. Whether this is a general situation will be studied further in other fluorenyllithium complexes solvated with appropriately chosen ligands.

Conclusions

The structure of the DEE complex of fluorenyllithium was determined by X-ray crystallography. This represents a new type of fluorenyl complex, further substantiating the proposals that the actual global minimum structure is dependent on the neutral ligand used. The reason for the change in the complex structure was investigated by quantum chemical calculations. In the optimal B3LYP/6-31G(d) structure of the fluorenyllithium ion pair, the Li atom is situated over the five-membered ring interacting in an η^5 fashion, **2a**. However, our computational study reveals that the optimal gas-phase structure of Li($C_{13}H_9$)(DEE)$_2$, **1a**, is similar to that in the crystal. From a comparison with the smaller complex Li($C_{13}H_9$)(H_2O)$_2$, it is concluded that intramolecular strain between the DEE ligands and the fluorenyl framework destabilize the ring-centered complex so that the structure with Li(DEE)$_2^+$ interacting with the C9 and C10 atoms (**1a**) becomes the global minimum, 1.9 kcal/mol lower in energy than the η^5 complex (**1b)** at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level. This also indicates that the use of water as a model for ether ligands is reasonable from an electronic point of view but that important intramolecular steric effects cannot be accounted for by this model.

Experimental Section

Preparation of [Li($C_{13}H_9$)(DEE)$_2$] (1). All experiments were carried out under an argon atmosphere. Fluorene was purchased from Aldrich and used without further purification. *n*-Butyllithium (2.5 M) was purchased from Acros Chimica, and the concentration was determined by titration with 1-pyreneacetic acid prior to use.[14] The solvents were dried by refluxing with potassium (hexane) or a sodium−potassium alloy (DEE) immediately before use.

Fluorene (75 mg, 0.45 mmol) was dissolved in 5 mL of a 1:1 mixture of hexane/DEE. The mixture was cooled in an ice bath, and 0.19 mL (0.47 mmol) of 2.5 M *n*-BuLi in hexane was added dropwise to the stirred solution. A massive yellow precipitate was formed immediately. The solution was transferred with a cannula at 0 °C into a glass ampule. The ampule was sealed off and slowly cooled to −20 °C. This resulted in the formation of needle-shaped crystals.

X-ray Crystallography. A colorless crystal fragment was isolated, cut, and mounted by the use of low-temperature techniques[15] (under argon at −150 °C) and transferred in Lindemann capillaries under liquid nitrogen to the diffractometer. Diffracted intensities were measured with a Rigaku AFC6R diffractometer using radiation from a RU200 rotating anode source operating at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. The intensities of three reflections monitored regularly after measurement of 150 reflections confirmed crystal stability

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[14] Kiljunen, H.; Hase, T. A. *J. Org. Chem.* **1991**, *56*, 6950.
[15] Håkansson, M. *Inorg. Synth.*, in press.

during data collection. Corrections were made for Lorentz, polarization, and absorption effects. The structure was solved by direct methods (SHELXS)[16] and refined using SHELXL,[16] using full-matrix least-squares calculations on F^2, including anisotropic thermal parameters for the lithium, carbon, nitrogen, and oxygen atoms. All hydrogen atoms were located from difference maps and refined isotropically. Structural illustrations have been drawn with Ortep-3 for Windows.[17]

Computational Methods. Semiempirical calculations were carried out with the MNDO[18] and PM3[19] methods, as implemented in Spartan 4.1.1.[20] Successive Hartree−Fock (HF) calculations were performed with the 3-21G and 6-31G(d) basis sets of Pople and co-workers,[21] which are of valence double-ζ quality. The ab initio calculations were carried out with the Gaussian94 program package.[22] To investigate the character of the computed stationary points of the potential-energy surface, frequency calculations were carried out at the HF/3-21G level. The results were improved by density functional theory using the three-parameter hybrid functional of Becke for the exchange part combined with the nonlocal gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP).[23] Geometry optimizations were carried out at the B3LYP6-31G(d) level. Subsequent B3LYP single-point energy calculations were carried out with the 6-31+G(d) basis set, which has diffuse basis functions added to second-row atoms.

Acknowledgment. Financial support from the Swedish Natural Science Research Council is gratefully acknowleged. The computational part of the project was carried out on the CRAY C90 computer of the Nationellt Superdatorcentrum (NSC) in Linköping, Sweden. C.-H.O. is grateful to NSC for the allotment of computer time.

Supporting Information Available: Tables of refined atomic coordinates, calculated atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and with calculated energies and geometry data at the B3LYP/6-31G(d) level (26 pages). Ordering information is given on any current masthead page.

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[16] Sheldrick, G. M. *SHELXS-86 and SHELXL-93*; University of Göttingen: Göttingen, Germany, 1986 and 1993.

[17] Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, 565.

[18] Dewar, M.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

[19] (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Lithium parameters from Anders, E.; Koch, R.; Freunscht, P. *J. Comput. Chem.* **1993**, *14*, 1301.

[20] *Spartan Version 4.1*; Wavefunction Inc.: Irvine, CA, 1996.

[21] (a) Binkley, J. A.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[22] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. W. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen. W.; Wong, M. W.; Andres, J. L.; Repogle, R. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94, Revision C.3*; Gaussian Inc.: Pittsburgh, PA, 1995.

[23] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.