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Molecular Structure of Fluorenyllithium[†,‡]

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The orange precipitate obtained after the well-known preparation of fluorenyllithium was recrystallized from a solution of benzene or toluene in order to get orange-red crystals which were of sufficient quality for X-ray diffraction. By this procedure we succeeded in redetermining the molecular structure of a donor-free unsubstituted fluorenyllithium compound, which might be the smallest alkali-metal compound containing a donor-free cyclopentadienyl-like ligand within an annelated ring system to date. The description of the bonding situation is based on *ab initio* calculations as well as on a comparison with analogous compounds.

Introduction

The special kinds of interactions between Li^+ cations and Cp^- anions or its derivatives have been intensively studied for many years.[1] Very recently the solid-state structure of donor-free LiCp has been obtained by powder diffraction methods and can be described as a chainlike Li−Cp−Li−Cp arrangement.[2] Furthermore, the first Li sandwich compound, $[LiCp_2]^-$,[3] and $LiCp^B$, forming dimeric units,[4] were both studied by single-crystal X-ray diffraction. Besides these investigations of the solid-state structures, many quantum-chemical results were published that—nearly without any exception—refer to monomeric species. However, if additional donor molecules are coordinated, e.g. tmeda, several monomeric species could be structurally characterized for which interactions between Li^+ cations and aromatic five- or six-membered-ring systems within condensed ring compounds exhibiting aromatic character are observed.[1] However, the Li−arene interactions, which are of particular interest, are modified in the presence of donor molecules and therefore cannot be compared with results from quantum-chemical calculations neglecting the donor component.[5] Thus, special attention was focused on the preparation of monomeric or at least dimeric donor-free Li−arene systems.[6] Besides the two above-mentioned Cp derivatives, $[LiCp_2]^-$ and $LiCp^B$, in this series also $[(isodiCp)_2Li]^-$ [7] and [7b*H*-indeno[1,2,3:*j*,*k*]fluorenyl]lithium (**2**)[8] are known, the latter of which exhibits a sandwich-like molecular structure including an annelated carbon ring system: two Li^+ cations are both coordinated by the six-membered rings of each indenofluorenyl unit. In addition to these examples we have now succeeded in the structural analysis of fluorenyllithium (**1**) by X-ray techniques.[9] On this basis Li−arene η^6- and η^5-interactions can be compared in a simple manner. As **1** represents an often-used reagent in organometallic chemistry, the results presented here will be of general interest.

Results and Discussion

As shown by the X-ray crystal structure determination of **1**, the asymmetric unit consists of one $C_{13}H_9Li$

[†] Dedicated to Prof. B. Krebs on the occasion of his 60th birthday.

[‡] Abbreviations. Bz, benzyl (CH_2Ph); Cp^B, pentabenzylcyclopentadienyl ($C_5(CH_2Ph)_5$); isodiCp, isodicyclopentadienyl ($C_{10}H_{11}$); $Cp_c/C_{6(c)}$, center of a Cp or a six-membered ring; tmeda, tetramethylethylenediamine.

(1) (a) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903−3907. (b) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339−7346. (c) Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 737−743. (d) Youngs, W. J.; Djebli, A.; Tessier, C. A. *Organometallics* **1991**, *10*, 2089−2090. (e) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7346−7351. (f) Bladauski, D.; Rewicki, D. *Chem. Ber.* **1977**, *110*, 3920−3929. (g) Malaba, D.; Chen, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1992**, *11*, 1007−1009. (h) Håkansson, M.; Ottosson, C.-H.; Boman, A.; Johnels, D. *Organometallics* **1998**, *17*, 1208−1214.

(2) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855−3858.

(3) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744−1745.

(4) Dohmeier, C.; Baum, E.; Ecker, A.; Köppe, R.; Schnöckel, H. *Organometallics* **1996**, *15*, 4702−4706.

(5) There are further compounds, in which "classically" bonded Li^+ ions form additional inter- or intramolecular Li−arene interactions. Though these interactions with respect to the distances are similar to those in the species described here, the former ones should not be discussed here because a separation of different interactions at the same Li atom—similar to the above-mentioned donor-stabilized arene complexes—is not possible: (a) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353−11357. (b) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2150−2151. (c) Gemünd, B.; Nöth, H.; Sachdev, H.; Schmidt, M. *Chem. Ber.* **1996**, *129*, 1335−1344.

(6) (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781−4788. (b) Waterman, K. C.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3138−3140. (c) Blom, R.; Faegri, K., Jr.; Midtgaard, T. *J. Am. Chem. Soc.* **1991**, *113*, 3230−3235 and literature cited therein. (d) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075−7083.

(7) (a) Zargel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 6466−6467.

(8) Crystals of [7b*H*-indeno[1,2,3:*j*,*k*]fluorenyllithium contain half a molecule of benzene per formula unit: (a) Bladauski, D.; Dietrich, H.; Hecht, H.-J.; Rewicki, D. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 474. (b) Bladauski, D.; Broser, W.; Hecht, H.-J.; Rewicki, D.; Dietrich, H. *Chem. Ber.* **1979**, *112*, 1380−1391.

(9) After this paper had been accepted for publication, we became aware of a preliminary description of the structure of lithium fluorenide, which was not included in the Cambridge Data File, though this short publication is 15 years old: Schmidt, H.-J.; Rewicki, D. *Acta Crystallogr.* **1984**, *A40*, C293. A transformation of coordinates of the cell dimensions presented in this former paper shows that this structure is in principle identical with that discussed in the present paper.

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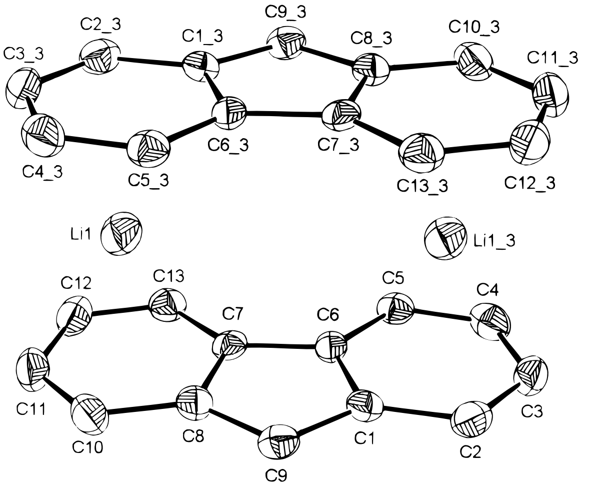


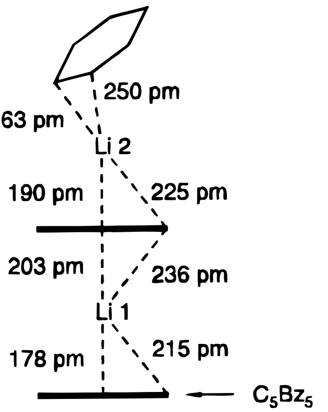
Figure 1. Molecular structure of **1c** (ORTEP drawing; thermal ellipsoids on the 50% probability level; H atoms omitted). Selected distances (Å) and angles (deg): Li−Li′, 4.345(9); Li′−C1, 2.5010(80); Li′−C2, 2.451(7); Li′−C3, 2.362(7); Li′−C4, 2.322(7); Li′−C5, 2.367(7); Li′−C6, 2.432(7); Li−C7, 2.429(7); Li−C8, 2.491(7); Li−C10, 2.461(7); Li−C11, 2.376(7); Li−C12, 2.336(7); Li−C13, 2.365(7); C1−C6, 1.453(5); C1−C2, 1.423(5); C2−C3, 1.385(5); C3−C4, 1.410(5); C4−C5, 1.377(5); C5−C6, 1.408(4); C6−C7, 1.428(5); C7−C8, 1.449(5); C8−C9, 1.408(5); C1−C9, 1.410(5); C10−C11, 1.375(5); C11−C12, 1.422(6); C12−C13, 1.376(5); C7−C13, 1.405(5); C8−C10, 1.419(5).

subunit. **1** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$). The lattice is built up of subunits in which two lithium ions are encapsulated by two nearly planar and parallel arranged carbanions; i.e., they form sandwich-shaped dimeric units, $(C_{13}H_9Li)_2$ (Figure 1).[10] The carbanions of this dimeric unit reveal an anti arrangement; the Li^+ ions are η^6-coordinated by the six-membered rings. The average Li−C distance is 2.408 Å, and the distances of the ring centers to their Li^+ ions are $d(Li-C_{6(c)}) = 1.9570(70)$ Å and 1.9510(70) Å, respectively; i.e., the distance between these ring centers is 3.90 Å, and the Li^+ ions occupy a position that is nearly in the middle of the direct line connecting these centers. The Li−Li distance in this dimeric unit is 4.345(9) Å; the average C−C bonding length is 1.41 Å.

The mean Li−C distances in **1** and **2** are nearly identical (2.408 and 2.41 Å, respectively), which means that the Li−arene bonding situations in both compounds are comparable, though in contrast to **2** no solvent molecules are included in the crystals of **1**.[8] Consequently, no structure-determining interactions should be based on the solvent molecules.

In the most simple main-group-metal sandwich complex, the lithocene anion ($[LiCp_2]^-$), the average Li−C distance (2.318(4) Å) is shorter than that in **1**, but the Cp_c-Li distance (2.008(4) Å) is longer than the $C_{6(c)}$-Li distance in **1**.[3,11]

Chart 1. Schematic Representation of the Bonding Situation in (Pentabenzylcyclopentadienyl)lithium, $[\{(\eta^5\text{-}C_5Bz_5)Li\}_2(C_6D_6)](C_6D_6)_2$[4]



The shortest Li−C distance within Li−arene π-bonded molecules is observed in dimeric $LiCp^B$ ($Li-C_{Cp}$ = 2.11(2)−2.19(2) Å; average 2.15 Å). Also, the $Li-Cp^B{}_c$ distance in this compound (1.78 Å) seems to represent a minimum value in such systems, which is exceeded by the analogous distances of most of the monomeric compounds obtained by means of quantum chemical calculations. In Chart 1 this special bonding situation of dimeric $LiCp^B$ is outlined to depict in a clear manner the different Li−arene interactions discussed here.

To get better insight into the distinct bonding state of dimeric fluorenyllithium, quantum-chemical calculations were performed on monomeric compounds exhibiting η^6- and η^5-coordinated Li (**1a**/**1b**) as well as on the dimeric species **1c** observed in the crystal (Chart 2). As expected, our DFT calculations on **1a** and **1b** confirm the results published very recently by Schleyer *et al.*[6d] These calculations on **1a** and **1b** gain particular importance by the additional quantum-chemical results obtained for **1c**, because the theoretical and experimental data for **1c** correspond very well. Thus, the conclusion on the reliability of the theoretical results for the monomeric compounds **1a** and **1b**, which are not available experimentally, is supported. Consequently, also the energy values determined with the help of these quantum-chemical calculations should present a reliable basis for the interpretation of the bonding situation (Chart 3): energetically the monomeric η^5-bound species **1b** is clearly favored, compared with the η^6-bonded molecule **1a**, by 24 kJ mol^{-1}. Since there is no suitable donor molecule to complete the coordination sphere of the Li atom in **1b**, this species cannot be stabilized. A dimerization of **1b** to **1d** would result in an additional energy drop of about 63 kJ mol^{-1}. However, much more energy (223 kJ mol^{-1}) can be gained if two **1a** species (though of higher energy than **1b**) dimerize to **1c**. **1c** is favored against **1d** by 112 kJ mol^{-1}, because in the latter the coordination sphere of one Li atom is not completed.

The experimental and theoretical results presented in this paper extend the idea of the peculiar bonding situation in Li−arene compounds. However, in addition to the recently published quantum-chemical results concerning Li NMR shifts[6d] further detailed experimental studies have to be performed by means of Li NMR spectroscopy in order to investigate **1**. With the help

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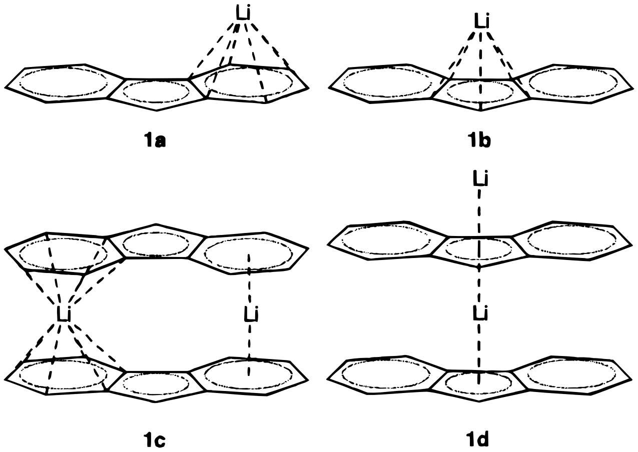
(10) Investigations of more soluble fluorenyllithium compounds such as [9-(2-hexyl)fluorenyl]lithium gave evidence of dimeric units, for which on the basis of Li NMR data (high-field-shifted signals) a sandwich-like structure has been postulated: (a) Exner, M. M.; Waack, R.; Steiner, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 7009−7018. (b) Takaki, U.; Collins, G. L.; Smid, J. *J. Organomet. Chem.* **1978**, **145**, 139−149.

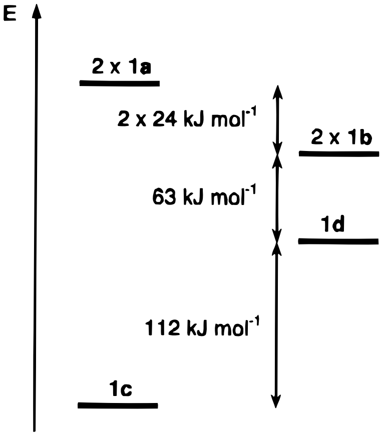
(11) In comparison with $[LiCp_2]^-$ the shorter distance between the ring planes in **1** is based on reduced electrostatic repulsion while the longer Li−C distance in **1** is attributed to the larger size of a six-membered-ring system in contrast to a five-membered one.

Chart 2. Molecular Structures of the Calculated Species 1a−d[a]



[a] Calculated Li−C distances (Å) (the numbering scheme of the fluorenyl carbon atoms is in agreement with that in Figure 1) are as follows: **1a**: 2.173 (Li‴−C4′/C12‴); 2.189 (Li‴−C3′/C11‴); 2.214 (Li‴−C5′/C13‴); 2.235 (Li‴−C2′/C10‴); 2.237 (Li‴−C6′/C7‴); 2.266 (Li‴−C1′/C8‴); 2.219 (mean value). **1b**: 2.179 (Li−C6/C7); 2.153 (Li−C1/C8); 2.113 (Li−C9); 2.155 (mean value). **1c**: 2.359 (Li′−C12′/C4‴); 2.361 (Li‴−C4′/C12‴); 2.378 (Li‴−C3′/C11‴); 2.379 (Li′−C11′/C3‴); 2.422 (Li′−C13′/C5‴); 2.426 (Li‴−C5′/C13‴); 2.466 (Li‴−C2′/C10‴); 2.468 (Li′−C10′/C2‴); 2.490 (Li′−C7′/C6‴; Li‴−C6′/C7‴); 2.535 (Li‴−C1′/C8‴); 2.536 (Li′−C8′/C1‴); 2.443 (mean value). **1d**, sandwiched Li atom, ring below: 2.160 (Li−C9); 2.233 (Li−C1/C8); 2.303 (Li−C6/C7); 2.246 (mean value). **1d**, sandwiched Li atom, ring above: 2.344 (Li−C9); 2.546 (Li−C1/C8); 2.879 (Li−C6/C7); 2.639 (mean value). **1d**, half-sandwiched Li atom, ring above: 2.135 (Li−C9); 2.159 (Li−C1/C8); 2.192 (Li−C6/C7); 2.167 (mean value).

Chart 3. Representation of the Energetic Situation of the Calculated Species 1a−d Mentioned in the Text



of such investigations it should be possible to decide whether the species detected in the solid state as well as those postulated by quantum-chemical calculations can also be present in solution. To find all possible molecules in these systems, e.g. a reaction product of **1d** with an aromatic solvent molecule, these extended spectroscopic studies have to be supported by theoretical investigations, e.g. by the calculation of Li NMR shifts of the above-mentioned species.

Experimental Section

General Comments. All manipulations were performed under anhydrous and anaerobic conditions by using Schlenk techniques or a glovebox (MBraun). Toluene and benzene were dried (sodium or potassium/sodium alloy), distilled, and degassed prior to use. *n*-BuLi (1.6 M in hexane) was used as received.

Table 1. Data for the X-ray Structural Study of $(C_{13}H_9)_2Li$

formula	$C_{13}H_9Li$
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
fw	172.14
a, Å	6.170(2)
b, Å	11.319(3)
c, Å	12.979(4)
α, deg	90
β, deg	96.22(3)
γ, deg	90
Z	4
V, Å^3	901.1(4)
ρ(calcd), g cm^{-3}	1.269
cryst dimens, mm	0.2 × 0.25 × 0.4
F(000)	360
μ, mm^{-1}	0.069
2θ range, deg	6.32−50.00
no. of rflns collct	1425
no. of indepdt rflns	1425
no. of rflns obsd	1038 ($F > 4\sigma(F)$)
no. of params	136
GOF	1.177
wR2 (all data)	0.1568
R1 ($F > 4\sigma(F)$)	0.0812
largest diff peak, e Å^{-3}	0.193
deepest diff peak, e Å^{-3}	−0.177

Synthesis of $\{C_{13}H_9Li\}_2$ (1). To a stirred solution of fluorene ($C_{13}H_{10}$) in toluene was added dropwise an equivalent portion of *n*-BuLi at dry ice temperature. The solution was warmed to room temperature and stirred for another couple of hours. After that the mixture was refluxed for a few minutes. The volatile compounds were removed *in vacuo* at room temperature. Recrystallization from benzene or toluene afforded noncrystalline material, in addition to some orange-red crystals.

X-ray Crystallographic Study. The crystals were removed from the Schlenk tube under a stream of argon and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the STOE STADI IV diffractometer. The data were collected at 200(2) K with Mo Kα radiation (graphite monochromated, $\lambda = 0.710\,69$ Å): ω scan mode, index ranges $-7 \le h \le 7$; $0 \le K \le 13$; $0 \le L \le 15$. The structure was solved by direct methods (SHELXS-90)[12a] and refined by full-matrix least-squares techniques. Hydrogen atoms: riding model, fixed isotropic U (SHELXL-93).[12b] Weighting scheme: $w^{-1} = \sigma^2F_o^2 + (0.0167P)^2 + 1.1958P$, $P = (F_o^2 + 2F_c^2)/3$. For further details see Table 1.

Quantum-Chemical Calculations. All DFT calculations were carried out using the TURBOMOLE[13a] set of programs. For the density functional we selected the B3-LYP parametrization.[13b] We employed the 6-31G* basis sets augmented with d-type polarization functions for Li (η(Li) = 0.2) and C (η(C) = 0.8). Although the experimentally deduced structural data were nicely reproduced using these basis sets, the lithium basis set (10s4p1d [3s2p1d]) seems to be highly unbalanced. DFT and SCF test calculations on the molecule LiCp show an unexpected influence of the flat d-type polariza-

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[12] (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473. (b) Sheldrick, G. M. Universität Göttingen, 1993.

[13] (a) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169. b) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem Phys. Lett.* **1995**, *240*, 283; **1995**, *242*, 652.

tion function of Li on the Li−C distance: B3LYP/6-31G*, 211.6 pm; SCF/6-31G*, 213.7 pm; B3LYP/6-31G* (no d on Li), 212.4 pm; SCF/6-31G** (no d on Li), 214.7 pm.

1a: symmetry, C_1; energy (total), −507.988 423 au. **1b**: symmetry, C_s; energy (total), −507.997 548 au. **1c**: symmetry, C_2; energy (total), −1016.061 601 au. **1d**: symmetry, C_s; energy, −1 016.018 823 au (1 au ≙ 1 hartree ≙ 2625.5 kJ mol^{-1}).

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles and two additional SCHAKAL views of fluorenyllithium (10 pages). Ordering information is given on any current masthead page.

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