Crystal Structure of [2-(Dimethylamino)-6-(*tert*-butoxy)phenyl]lithium

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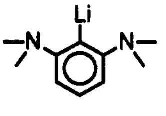
The structure of [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (**3**), determined by single-crystal X-ray diffraction (crystal data: monoclinic, $a = 10.891$ (1), $b = 16.984$ (1), and $c = 20.704$ (1) Å; $\beta = 100.6$ (1)°; $V = 3764$ (1) Å^3; space group $P2_1/n$; $(C_{12}H_{18}ONLi)_3$; $Z = 4$), reveals a trimeric aggregate with fully asymmetric lithium coordination. NMR provide evidence for a similar asymmetric structure in solution. The behavior of the C–Li coupling shows a dynamic trimer to be present at room temperature (a rarity in organolithium chemistry). This trimer becomes static at lower temperatures. The extreme distortion of the aryl rings from hexagonal geometry in **3** as in phenyllithium derivatives in general (CCC angles at lithium average 112.5°) is attributed to rehybridization of the lithiated carbon; a very low $^1J(^{13}C,^{13}C)$ of 27.8 Hz results.

Introduction

Trimeric organolithium compounds are rare. We published the first structure of trimeric [2,6-(dimethylamino)phenyl]lithium (**1**) in 1989.[1] A subsequent paper described the intramolecular O–Li bonding characteristics in the second trimeric organolithium compound: [2,6-(di-*tert*-butoxy)phenyl]lithium (**2**).[2]

This work deals with the structural features of a hybrid of **1** and **2**, i.e., [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (**3**), as deduced by X-ray analysis, NMR, and model ab initio computations.



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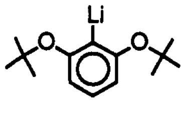

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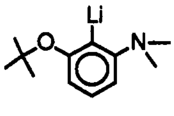

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X-ray Structure

The X-ray structure of [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (**3**), not unexpectedly, reveals the third example of a trimeric organolithium compound. The structure, depicted in Figure 1, shows a triangular arrangement of the three lithium cations, which are bridged by aryl anions (fractional coordinates, bond distances, and selected bond angles are given in Tables I and II, respectively). No fundamental differences with the structures of **1** and **2** are apparent. However, the symmetry of **3** is quite unexpected. The structure of **1** is propeller-like with a pseudothreefold symmetry axis.[1] The structure of **2** is similar but with somewhat unsymmetrical *tert*-butoxylithium coordination.[2] The lithium coordination in **3** is completely asymmetric: Li1 is intramolecularly solvated by two NMe$_2$ groups, Li2 is solvated by one NMe$_2$ group and one *t*-BuO group, and Li3 is solvated by two *t*-BuO groups. No explanation for this preferred asymmetry is obvious. The van der Waals interactions in the asymmetric trimer evidently are responsible; i.e., the asymmetry originates from better intraaggregate packing effects.

Table I. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for [2-(Dimethylamino)-6-(*tert*-butoxy)phenyl]lithium

atom	*x*	*y*	*z*	*U*(eq)
O(1)	0.4276 (2)	0.2040 (1)	0.42335 (7)	0.0542 (5)
O(2)	0.5773 (2)	0.3814 (1)	0.15251 (8)	0.0591 (6)
O(3)	0.6851 (2)	0.3129 (1)	0.41902 (8)	0.0662 (6)
N(1)	0.2303 (2)	0.4310 (1)	0.3113 (1)	0.0590 (7)
N(2)	0.1676 (2)	0.2961 (1)	0.1773 (1)	0.0540 (7)
N(3)	0.6457 (2)	0.2104 (1)	0.2029 (1)	0.0434 (7)
C(11)	0.3277 (2)	0.3149 (1)	0.3655 (1)	0.0464 (7)
C(12)	0.3394 (2)	0.2655 (1)	0.4203 (1)	0.0479 (7)
C(13)	0.2813 (2)	0.2770 (1)	0.47406 (7)	0.066 (1)
C(14)	0.1992 (2)	0.3409 (1)	0.47119 (7)	0.077 (1)
C(15)	0.1795 (2)	0.3915 (1)	0.41778 (7)	0.065 (1)
C(16)	0.2449 (2)	0.3775 (1)	0.3674 (1)	0.0499 (7)
C(17)	0.3838 (3)	0.1231 (1)	0.4105 (1)	0.0629 (9)
C(18)	0.2916 (3)	0.1195 (2)	0.3468 (2)	0.099 (1)
C(19)	0.3277 (4)	0.0914 (2)	0.4674 (2)	0.118 (2)
C(21)	0.3731 (2)	0.3420 (1)	0.1669 (1)	0.0474 (7)
C(22)	0.4500 (2)	0.3672 (1)	0.1241 (1)	0.0521 (8)
C(23)	0.4156 (3)	0.3712 (2)	0.0561 (1)	0.069 (1)
C(24)	0.2949 (3)	0.3534 (2)	0.0283 (1)	0.081 (1)
C(25)	0.2108 (3)	0.3303 (2)	0.0671 (1)	0.071 (1)
C(26)	0.2516 (2)	0.3238 (1)	0.1349 (1)	0.0501 (8)
C(27)	0.6230 (3)	0.4610 (2)	0.1638 (2)	0.075 (1)
C(28)	0.6030 (5)	0.5115 (3)	0.1035 (2)	0.151 (2)
C(29)	0.7600 (4)	0.4502 (3)	0.1936 (3)	0.150 (2)
C(31)	0.6677 (2)	0.2629 (1)	0.3123 (1)	0.0482 (7)
C(32)	0.7482 (2)	0.2828 (1)	0.3703 (1)	0.0547 (8)
C(33)	0.8753 (3)	0.2702 (2)	0.3825 (2)	0.074 (1)
C(34)	0.9277 (3)	0.2393 (2)	0.3322 (2)	0.075 (1)
C(35)	0.8564 (3)	0.2180 (2)	0.2739 (1)	0.0611 (9)
C(36)	0.7273 (2)	0.2286 (1)	0.2651 (1)	0.0498 (8)
C(37)	0.7241 (3)	0.3857 (2)	0.4549 (1)	0.074 (1)
C(38)	0.7539 (5)	0.4475 (2)	0.4090 (2)	0.134 (2)
C(39)	0.8311 (3)	0.3705 (2)	0.5116 (2)	0.104 (2)
C(110)	0.5018 (3)	0.0781 (2)	0.4047 (2)	0.097 (2)
C(111)	0.3259 (4)	0.4925 (2)	0.3233 (2)	0.104 (2)
C(112)	0.1041 (4)	0.4647 (3)	0.2936 (2)	0.116 (2)
C(210)	0.5569 (4)	0.4987 (3)	0.2150 (2)	0.132 (2)
C(211)	0.1668 (3)	0.2099 (2)	0.1805 (2)	0.078 (1)
C(212)	0.0387 (3)	0.3252 (2)	0.1594 (2)	0.093 (2)
C(310)	0.6095 (4)	0.4080 (2)	0.4825 (2)	0.112 (2)
C(311)	0.5676 (3)	0.1422 (2)	0.2060 (2)	0.089 (1)
C(312)	0.7056 (3)	0.2074 (2)	0.1453 (1)	0.096 (2)
Li(1)	0.2983 (4)	0.3400 (3)	0.2585 (2)	0.055 (1)
Li(2)	0.5482 (4)	0.3083 (3)	0.2250 (2)	0.058 (2)
Li(3)	0.5190 (4)	0.2745 (3)	0.3667 (2)	0.059 (1)

The asymmetry influences the lithium coordination geometry shown in Figure 2. Table III compares the lithium coordination in trimers **1**–**3**. The smaller variation in the O–Li bond distances in **3** is due to smaller differ-

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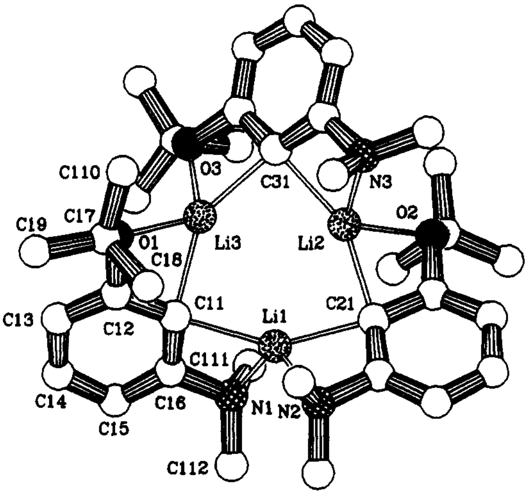

Figure 1. X-ray structure of [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (3). The full systematic numbering for molecule 1 is shown; the first digit gives the molecule number and the last digit(s) the atom number.

Table II. Bond Distances (Å) and Selected Bond Angles (deg) for [2-(Dimethylamino)-6-(*tert*-butoxy)phenyl]lithium

molecule no.	*X* = 1	*X* = 2	*X* = 3
C*X*1–C*X*2	1.398 (3)	1.394 (3)	1.392 (3)
C*X*2–C*X*3	1.391 (3)	1.389 (3)	1.377 (4)
C*X*3–C*X*4	1.401 (2)	1.368 (5)	1.379 (4)
C*X*4–C*X*5	1.385 (2)	1.382 (4)	1.359 (4)
C*X*5–C*X*6	1.387 (3)	1.396 (3)	1.396 (4)
C*X*6–C*X*1	1.400 (3)	1.401 (3)	1.396 (3)
C*X*2–O*X*	1.413 (3)	1.423 (3)	1.416 (3)
O*X*–C*X*7	1.463 (3)	1.445 (4)	1.463 (4)
C*X*7–C*X*8	1.506 (4)	1.497 (5)	1.492 (5)
C*X*7–C*X*9	1.522 (5)	1.517 (6)	1.516 (5)
C*X*7–C*X*10	1.519 (5)	1.528 (5)	1.515 (5)
C*X*6–N*X*	1.462 (3)	1.459 (3)	1.457 (3)
N*X*–C*X*11	1.463 (4)	1.464 (3)	1.444 (4)
N*X*–C*X*12	1.471 (5)	1.470 (4)	1.462 (4)
C*X*6–C*X*1–C*X*2	113.3 (2)	113.1 (2)	113.9 (2)
C*X*1–C*X*2–C*X*3	125.3 (2)	125.3 (2)	124.8 (2)
C*X*2–C*X*3–C*X*4	117.1 (2)	118.4 (3)	117.6 (3)
C*X*3–C*X*4–C*X*5	121.2 (2)	120.4 (3)	121.6 (3)
C*X*4–C*X*5–C*X*6	118.0 (2)	119.0 (3)	118.6 (3)
C*X*5–C*X*6–C*X*1	125.0 (2)	123.8 (2)	123.3 (2)
C*X*2–O*X*–C*X*7	119.4 (2)	120.4 (2)	122.2 (2)
C*X*6–N*X*–C*X*11	109.8 (2)	111.0 (2)	113.5 (2)
C*X*6–N*X*–C*X*12	113.5 (2)	114.5 (2)	115.9 (2)
C*X*11–N*X*–C*X*12	111.6 (3)	109.6 (2)	111.4 (2)
O*X*–C*X*2–C*X*1	116.1 (2)	116.3 (2)	113.0 (2)
O*X*–C*X*2–C*X*3	118.3 (2)	118.1 (2)	122.0 (2)
N*X*–C*X*6–C*X*1	115.2 (2)	115.4 (2)	114.9 (2)
N*X*–C*X*6–C*X*5	119.8 (2)	120.8 (2)	121.6 (2)

Table III. Comparison of the Lithium Coordination Geometry in the Trimers 1–3[a]

	ortho substituents		
	(1) NMe_2	(2) *t*-BuO	(3) NMe_2/*t*-BuO
C–Li	2.130–2.228 ⟨2.173⟩	2.139–2.188 ⟨2.159⟩	2.137–2.222 ⟨2.176⟩
N–Li	2.071–2.157 ⟨2.117⟩		2.070–2.127 ⟨2.101⟩
O–Li		1.984–2.111 ⟨2.038⟩	2.017–2.057 ⟨2.037⟩
Li···Li′	3.059–3.113 ⟨3.081⟩	2.962–3.074 ⟨3.029⟩	2.979–3.170 ⟨3.071⟩
N–Li–N′	113.3–119.3 ⟨116.1⟩		114.8
O–Li–O		108.4–111.6 ⟨109.8⟩	111.0
C–Li–C′	148.3–151.0 ⟨149.4⟩	147.1–152.3 ⟨150.5⟩	146.3–154.5 ⟨149.9⟩

[a] The range and ⟨averaged values⟩ are given in angstroms or degrees.

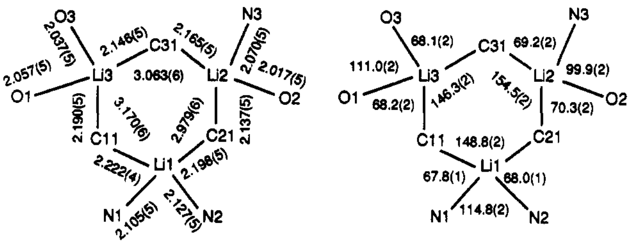

Figure 2. Lithium coordination geometry for [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (3). Left: bond distances (Å). Right: bond angles (deg).

ences in the orientation of the *t*-BuO substituents (this relationship was discussed extensively in the preceding paper).[2] The C–Li and N–Li distances are not affected, but somewhat larger variations in the nonbonding Li···Li′ distances and C–Li–C′ angles are found in 3. Thus, the asymmetry in 3 only affects bond angles in the nearly planar (maximum least-squares deviation 0.09 (1) Å) six-membered CLiC′Li′C″Li″ ring structure slightly. Although the C–Li bond length varies with the degree of lithium solvation[3] (i.e. number of solvent molecules and Lewis basicity of the solvent), we have not found a significant direct correlation between the experimental C–Li bond lengths and the type of solvation.

The structure of the anions (Table II) deserves comment. Although present in fairly rigid anions, the ortho heteroatoms (N and O) are bent a few degrees toward the Li core; i.e., the N–C and O–C bonds do not bisect the C–C–C angle. This can be deduced from the somewhat smaller N–C–C(Li) and O–C–C(Li) angles (average 115.2°) compared to the N–C–C(H) and O–C–C(H) angles (average 120.1°). Similar distortions have been found in 1 and 2. These document the strong driving force for intramolecular coordination.

The aryl rings in 3 are distorted markedly from the regular hexagonal geometry. Note the abnormally small CCC angles around the lithiated carbon atoms and the large CCC angles at the neighboring carbon atoms. Such anomalies, which are common in aryllithium structures, had been recognized earlier,[4,5] but no explanation was put forward. The phenomenon was described as being inherent to an aryl group bound to an electropositive metal.[4,5] We will discuss this subject below.

Structure in Solution

Crystals of 96% ^{6}Li-enriched [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (3) dissolve very well in toluene-d_8 (200 mg/mL). The ^{1}H NMR spectrum of 3 at 25 °C is straightforward (all NMR data are given in Table IV), but the ^{13}C spectrum at this temperature is complicated. The signal for the lithiated carbon atom shows a clean 1:3:6:7:6:3:1 C–Li coupling pattern with $J = 4.4$ Hz (Figure 3). Both this pattern and the coupling constant indicate that a ^{13}C nucleus is interacting with three ^{6}Li nuclei. This is characteristic of the four-center two-electron bonding found in tetrameric organolithium compounds.[6,7] Although it is possible that different aggre-

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Table IV. ^{1}H and ^{13}C NMR Data for 1-(Dimethylamino)-3-(*tert*-butoxy)benzene and [2-(Dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (3)[a]

^{1}H NMR Data

	H1	H3	H4	H5	NMe$_2$	*t*-BuO
X = H, C_6D_6, 25 °C	6.45	6.41	7.10	6.51	2.53	1.29
X = Li, toluene-d_8, 25 °C		6.77 (d, 7.8)	7.12 (t, 7.8)	6.77 (d, 7.8)	2.59 (s)	1.22 (s)
X = Li, toluene-d_8, −5 °C		6.81 (d, 7.7)	7.19 (t, 7.7)	6.83 (d, 7.7)	2.62 (s)	1.21 (s)
X = Li, toluene-d_8, −70 °C		6.83 (br)	7.22 (br)	6.83 (br)	2.3–3.0 (br)	1.34/1.14 (br)

^{13}C NMR Data

	C1	C2	C3	C4	C5	C6	NMe$_2$	*t*-BuO
X = H, C_6D_6, 25 °C	108.2	157.2	109.2	129.3	112.6	152.0	40.3	29.2/77.4
X = Li, toluene-d_8, 25 °C	160.8[b]	165.4	110.6	127.5	113.1	163.5	45.7	29.4/76.8
X = Li, toluene-d_8, −5 °C	160.9[c]	165.3	110.6	127.4	113.1	163.2	45.6	29.2/76.6

[a] Chemical shifts in ppm and coupling constants (in parentheses) in hertz. Atom numbering corresponds to that in Figure 1. [b] ^{13}C–^{6}Li coupling constant 4.4 Hz. [c] ^{13}C–^{6}Li coupling constant 6.6 Hz.

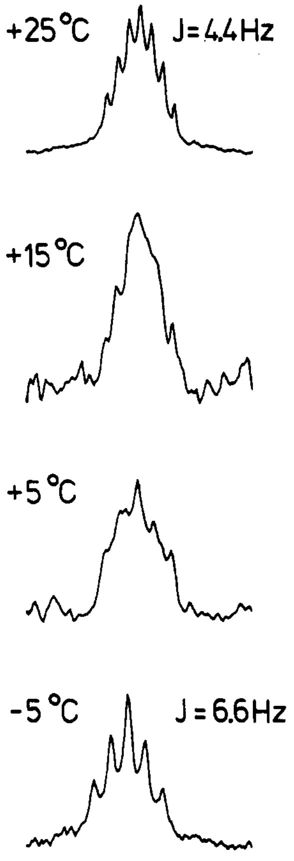

Figure 3. ^{13}C signal for the lithiated carbon in [^{6}Li]-[2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (3) at different temperatures.

gation states are present in the solid state and in solution, the existence of a dynamic aggregate appears to be the better explanation for the NMR behavior since an apolar solvent like toluene is not expected to interact strongly with lithium compounds. Hence, interaggregate exchange processes are slow enough to detect C–Li coupling, and the faster intraaggregate exchange processes give rise to visible coupling of the observed ^{13}C nucleus with all the Li atoms in the aggregate. This interpretation was confirmed by observing the change in the signal for the lithiated carbon atom at lower temperatures (Figure 3). Cooling the sample slows down the intraaggregate exchange, and the dynamic aggregate is converted into a static aggregate. The sharp septet (at 25 °C, Figure 3) changes first into a blurred septet (15 °C), then into a blurred quintet (5 °C), and finally into a smooth quintet (−5 °C). This quintet with intensity ratio 1:2:3:2:1 and ^{13}C,^{6}Li coupling constant of 6.6 Hz indicates a three-center two-electron bond, as observed in static dimers and trimers. The trimeric nature of 3 in an apolar solvent is confirmed by cryoscopy in benzene (n = 2.9, c = 0.12 molal). The 50% increase in the coupling constant agrees with the inversely proportional relationship of J with the number of Li-bonding partners.[7b]

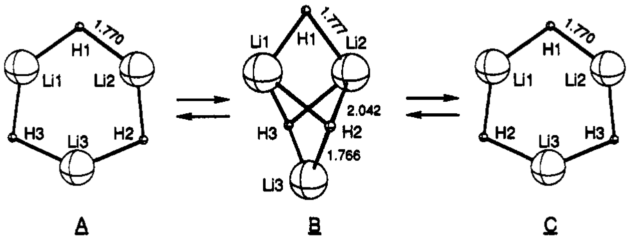

Figure 4. Possible mechanism for rapid exchange in the dynamic trimer; ab initio calculations, MP2-FU/6-31G*.[10] The LiH trimer A converts via transition structure B into trimer C. This process, with an activation energy of 16.4 kcal/mol, most likely accounts for the fast intraaggregate exchange of anions as found by NMR.

Whereas several examples of dynamic aggregates (tetramers[8] as well as hexamers[9]) have been found in alkyllithium chemistry, no examples in aryllithium chemistry have been reported yet. In light of the results with 3, we reexamined the C–Li coupling in the closely related trimers 1[1] and 2,[2] but no dynamic behavior could be detected. A possible mechanism for fast anion (or lithium) exchange in the dynamic trimer is evaluated by ab initio calculations on the simple $(LiH)_3$ model A, depicted in Figure 4.[10] Two anions (or cations) move synchronically out of the trimer plane, one upward and the other downward. In the transition structure B (which was confirmed by frequency analysis, NIMAG = 1), both the exchanging anions are involved in four-center two-electron bonding. According to the activation energy (calculated to be 16.4 kcal/mol, MP2-FU/6-31G*) such an exchange process is likely to proceed at room temperature.

Further cooling of the sample results in broadening of all ^{13}C resonances and splitting of the NMe$_2$ resonance (coalescence temperature −50 °C, $\Delta\nu$ = 576 Hz). The diastereotopicity of the *N*-methyl groups arises from the N–Li coordination which positions one methyl group in the $Li_3C(ipso)_3$ plane and the other out of this plane, just

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(10) MP2-FU/6-31G* optimized structures. LiH trimer A: D_{3h}, E = −24.144 11 hartree. LiH trimer B, C_S, E = −24.117 94 hartree.

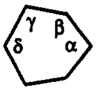
as observed in the X-ray structure (Figure 1). A similar situation has been reported for trimer 1.[1]

The ^1H resonances also broaden at lower temperatures. At −70 °C two broad signals in an approximately 1:2 ratio appear for the *tert*-butoxy group. This ratio suggests that the asymmetric conformation shown in Figure 1 is frozen out in solution at low temperature. The larger singlet arises from *t*-BuO(1) and *t*-BuO(3), which are nearly equivalent, and the smaller singlet from *t*-BuO(2). The signal for the dimethylamino group is converted into a very broad "mountain-chain"-like spectral feature (ranging from 2.3 to 3.0 ppm) with at least three distinct maxima. This broad signal band must arise from the additional NMe in-plane/NMe out-of-plane diastereotopicity (which is also observed in the ^{13}C spectra) and should give at least four signals in a ratio of 2:2:1:1. We were not able to detect three distinct resonances in the low-temperature ^6Li spectrum, but extensive broadening of the ^6Li singlet (the half-height line width is 1 Hz at 25 °C and 25 Hz at −100 °C) indicates approach to a slow-exchange limit. Thus, it is most likely that the asymmetric trimer preferred in the solid state also exists in solution at low temperatures.

Nature of Ring Deformation in Aryllithium Compounds

The regular hexagonal geometry of the carbon skeleton of the benzene ring is modified by substitution.[11] These distortions arise from an increase (4) or decrease (5) of the endocyclic angle α. Distortions of the endocyclic angles β follow as a necessary requirement to preserve ring planarity.

4



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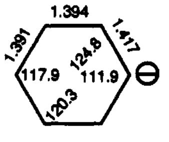

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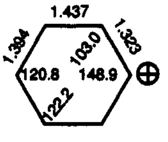

7

Domenicano et al. showed that a linear correlation exists between the angle α and the Pauling electronegativity of the ring-bound substituent atom.[11c,12] An electron-withdrawing substituent gives rise to α-angles larger than 120° and vice versa. Data from the Cambridge Structural Database[13] together with our own structural studies comprise 19 crystal structures of aryllithium compounds: all show large ring deformations. In these compounds, the α-angles range from 111.2 to 114.6° (average 112.5°) and the β-angles range from 121.6 to 126.2° (average 124.9°). This corresponds nicely with the MP2/6-31G* geometry of phenyllithium with an α-angle of 114.3° and β-angles of 123.4°. These large deviations from 120° due to lithium substitution agree with Domenicano's correlation and dominate the small deformations originating from other substituents which may be present. We have shown the same angular effects for isopropyl-X[14] and ethyl-X[15] compounds.

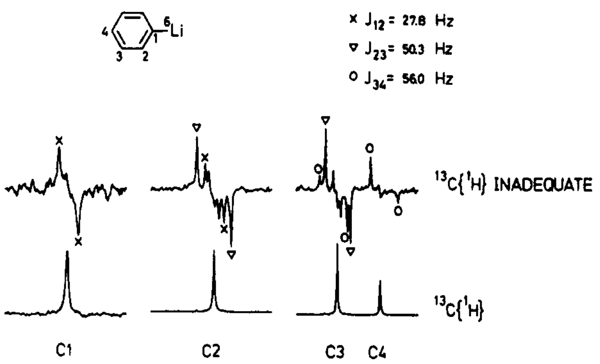

Figure 5. INADEQUATE ^{13}C spectrum[18] of phenyllithium in THF showing the $^1J(^{13}C,^{13}C)$. The small signals at the inside of the antiphase doublets arise from smaller two-bond couplings or are remnants of the surpressed single-quantum coherence.

The observed ring distortions have been discussed in terms of hybridization effects at the substituted carbon.[11c,12] According to Walsh's rule,[16] the p-character tends to concentrate in the hybrid orbital directed toward the most electronegative substituent (this follows from the fact that p-electrons are held more loosely than s-electrons). Thus an electropositive ring substituent increases the p-character in the bonds between the substituted carbon and its ring neighbors, resulting in a decrease of bond angle α.

This explanation should be confirmed by an additional elongation of C(ipso)–C bond distances. However, the experimentally observed changes in bond lengths are rather small in respect to the errors arising from rigid and nonrigid thermal motions. Despite correction procedures and low-temperature measurements, errors are still too large to obtain a significant correlation. These errors are eliminated in ab initio calculations. Calculations[17] on the utmost species in the series, the phenyl anion (*6*) and cation (*7*),[18] confirm the experimentally observed angle deformation and the expected bond length distortion.

Since $^1J(^{13}C,^{13}C)$ is very sensitive to the hybridization of both carbons,[19] we measured $^1J(^{13}C,^{13}C)$ in phenyllithium. This provided an experimental confirmation for the explained ring distortions. The one-bond $^{13}C,^{13}C$ coupling constants have also been related to the electronegativity of the substituent.[20] The recorded INADEQUATE ^{13}C spectrum[21] of phenyllithium in THF-d_8 is depicted in Figure 5. A very small coupling constant of 27.8 Hz is observed between C(1) and C(2), whereas the other one-bond coupling constants are hardly changed by lithium substitution. The C(1)–C(2) coupling constant is much smaller than that in benzene (57.0 Hz)[19] and is even smaller than the ethane (34.6 Hz)[19] and cyclobutane (29.8 Hz) values.[22] Although a linear relationship between $^1J(^{13}C,^{13}C)$ and the percentage s-character has been observed for single C–C bonds, the additional influence of orbital interaction and spin-dipolar noncontact coupling terms on coupling constants in unsaturated C–C bonds

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prohibits an quantitative estimation of the percentage of s-character in C_6H_5Li.[19] Nevertheless, the extremely low 27.8-Hz value (which to our knowledge is the lowest value ever observed for a $^1J(^{13}C,^{13}C)$ in a substituted benzene)[20,23] implies a considerable decrease in s-character in the involved bonding hybrids when compared to benzene. This is in agreement with our explanation for the observed ring distortion.

Conclusions

The crystal structure of [2-(dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (**3**) reveals a trimeric aggregate with asymmetric Li coordination. This asymmetry, which is also found in the solution, most likely originates from intramolecular interactions within the aggregate.

An NMR study shows a dynamic trimer to be present at room temperature. It is likely that the exchange mechanism proceeds via a trimeric aggregate in which two of the three anions are involved in four-center two-electron bonding (Figure 4). The extreme distortions of the aryl rings from regular hexagonal symmetry are related to rehybridization effects on the lithiated carbon atom. The extremely high s-character in the C–Li bond is supported by the very small $^1J(^{13}C,^{13}C)$ of 27.8 Hz involving the lithiated carbon and its ortho carbons.

Experimental Section

General Conditions. All experiments were carried out in an inert nitrogen atmosphere using Schlenk techniques and syringes. Solvents were freshly distilled from sodium/benzophenone prior to use.

NMR spectra were recorded on a Bruker AC 300 pulse spectrometer (^1H frequency 300 MHz). ^1H and ^{13}C chemical shifts are given with respect to TMS. For ^{13}C spectra, internal solvent signals were used for reference: benzene-d_6 (δ = 128.0 ppm) and toluene (CD_3, δ = 20.4 ppm).

Ab initio calculations were performed with the GAUSSIAN 90 program.[24]

Synthesis. [2-(Dimethylamino)-6-(*tert*-butoxy)phenyl]lithium (**3**) was obtained via direct metalation of 1-(dimethylamino)-3-(*tert*-butoxy)benzene by butyllithium in hexane under reflux conditions. Butyllithium (15.0 mL, 1.6 M in hexane, 24.0 mmol) was added to 1-(dimethylamino)-3-(*tert*-butoxy)benzene (4.5 g, 23.8 mmol) dissolved in 15.0 mL of hexane at room temperature. This solution was heated under reflux for 2 h, and the solvent was removed under reduced pressure. The remaining white solid was recrystallized from diethyl ether/pentane (1:2), yielding colorless single crystals (55%) suitable for X-ray diffraction and NMR analyses.

X-ray Data Collection. A suitable single crystal with dimensions 0.2 × 0.3 × 0.5 mm^3 was sealed under argon in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer (λ(Cu Kα) = 1.541 84 Å). The cell constants were determined by refining the setting angles of 25 reflections with θ in the range 19–25°. Crystal data: monoclinic, a = 10.891 (1), b = 16.984 (1), and c = 20.704 (1) Å; β = 100.6 (1)°; V = 3764 (1) Å; space group $P2_1/n$; $(C_{12}H_{18}ONLi)_3$; Z = 4, d_{calcd} = 1.055 g/cm^3. A total of 8239 unique reflections were collected at T = 22 °C within the Cu sphere up to θ = 75° ($0 \le h \le 13$, $0 \le k \le 21$, $-25 \le l \le 25$) of which 5748 reflections with $I \ge 2.5\sigma$ were considered to be observed. Standard reflections (041, 110, and 2-30) were measured every 50 reflections. Corrections for Lorentz polarization effects and linear decay were applied. On the basis of systematic extinctions, the space group was established to be $P2_1/n$. The structure was determined by direct methods (SHELXS-86). Full-matrix least-squares refinement with SHELX-76 (non-hydrogen atoms with anisotropic temperature factors; the hydrogen atoms were placed first on calculated positions and then refined with a riding model) converged to $R(F) = 0.068$ and $R(wF) = 0.075$ with $w = 1/\sigma^2(F)$ and 410 refined parameters.

Neutral atom scattering factors were used for all atoms.[25] Anomalous dispersion factors were taken from Cromer and Liberman.[26] Calculations were performed on a Micro Vax II computer using the SHELXS-86[27] and SHELX-76[28] programs and the EUCLID package[29] (geometry calculations and graphics).

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Supplementary Material Available: Tables of hydrogen atom positions, isotropic and anisotropic thermal parameters, bond distances, and bond angles for **3** (5 pages). Ordering information is given on any current masthead page.

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