

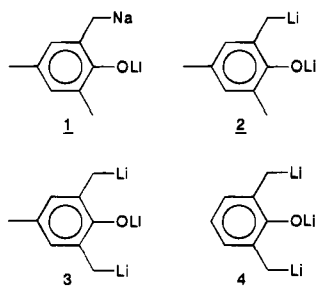
Crystal Structure of Trilithiated Dimethylphenol

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Recently, we published the first structure of a mixed organosodium/lithium alkoxide aggregate (1),¹ a model for a superbase system: BuLi/MO-Bu (M = Na, K).² In order to study the influence of the heavier alkali metal on the structure of mixed carbanion/alkoxide aggregates, we planned to make a direct comparison of 1 with the analogous dilithio compound (2). Unexpectedly, the reaction of 2,4,6-trimethylphenol with 2.2 equivs of BuLi/*N,N,N',N'*-tetramethylethylenediamine (tmeda) yielded crystals consisting of the trilithio compound 3•tmeda in 40% yield. A crystal structure determination of this highly lithiated aromatic compound failed due to substantial disorder of the whole structure. However, the structure determination of a slightly modified compound (4•tmeda)^{3,4} was successful.



Crystals of 4, obtained from a hot benzene/tmeda solution, show the composition (4•tmeda)₄(benzene)_{1.5} and crystallize in the centrosymmetric triclinic crystal system. The asymmetric unit contains two tetrameric aggregates of 4•tmeda (Figure 1) and about three disordered benzene molecules filling holes between aggregates but showing no coordinative interactions with the lithiums. Both independent tetrameric aggregates have similar structures with approximate (noncrystallographic) *S*₄ symmetry in which three different types of Li cations can be recognized. One of these units repeated by approximate *S*₄ symmetry is shown by atom numbering in Figure 2. The range and average of equivalent bond distances and angles in the two tetramers are summarized in Table 1. The small ranges show

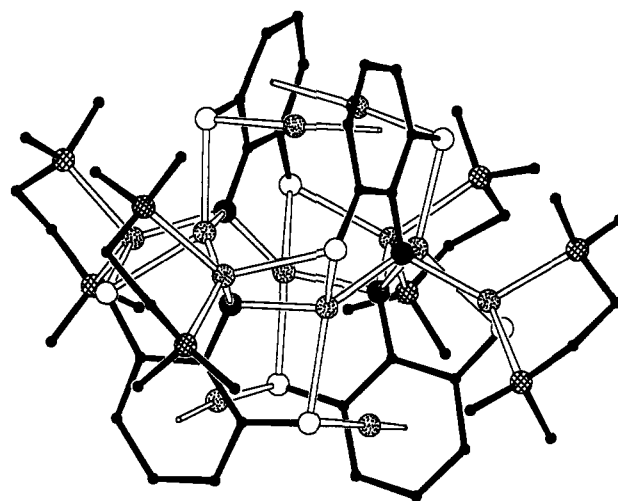


Figure 1. Structure of (4•tmeda)₄. The carbon framework is depicted as a stick model, and hydrogen atoms have been omitted for clarity (benzylic carbons are white, nitrogens cross-hatched, oxygens black, and lithiums dotted).

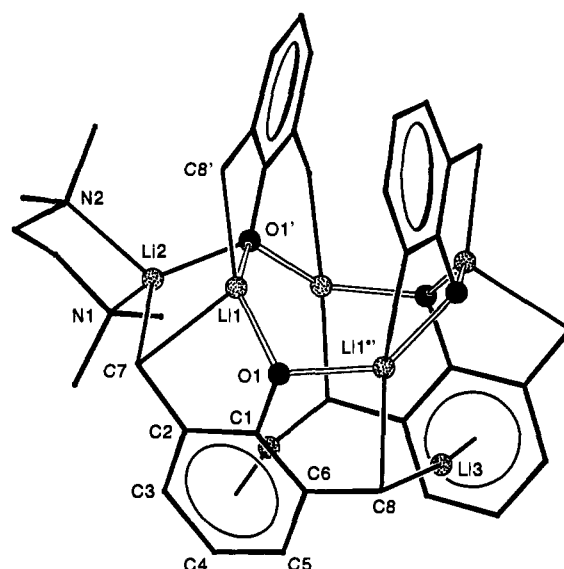


Figure 2. Partial structure showing the (O–Li)₄ ring and atom numbering for one of the units repeated by approximate noncrystallographic *S*₄ symmetry.

that both independent tetramers are structurally similar and are close to *S*₄ symmetry.

The core of the structure is formed by aggregation of the four lithium phenoxide functionalities. This O–Li tetramer-

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(3) Synthesis (under argon using Schlenk techniques): 5.00 g (40.9 mmol) of 2,6-dimethylphenol was dissolved in 90 mL of hexane and 20 mL of tmeda (133 mmol). The mixture was heated until reflux, and 85 mL of BuLi (1.6 M in hexane, 136 mmol) was slowly added via a syringe. Refluxing for 1 h resulted in a yellow-orange solution, which after slow cooling yielded crystals of 4•tmeda (8.91 g; yield, 81%). ¹H-NMR (THF-*d*₆, 250 Mhz, 25 °C): δ 0.81 (s br, 4H); 2.16 (s, 12H); 2.31 (s, 4H); 5.78 (d, ³J(H,H) = 6.8 Hz, 2H); 5.90 (t, ³J(H,H) = 6.8 Hz, 1H). ¹H-NMR (toluene-*d*₆, 250 Mhz, 0 °C): δ 1.34 and 1.64 (d, ²J(H,H) = 5.3 Hz, 1H, CH₂); 1.49 and 1.53 (s, 1H, CH₂); 2.09 (s br, tmeda); 6.15 (dd, ³J(H,H) = 7.3 Hz, ⁴J(H,H) = 2.0 Hz, 1H); 6.31 (dd, ³J(H,H) = 7.5 Hz, ⁴J(H,H) = 2.0 Hz, 1H); 6.46 (t, ³J(H,H) = 7.4 Hz, 1H). Crystals suitable for X-ray diffraction were obtained by recrystallizing from a hot benzene/tmeda(10%) mixture and slowly cooling to room temperature. NMR analysis of the crystals deuterated in methanol-*d*₄ shows a dimethylphenol/tmeda/benzene ratio of 1/1/0.35 δ 2.16 (t, ²J(H,D) = 2.0 Hz, 2H); 2.24 (s, 4H); 6.22 (t, ³J(H,H) = 7.3 Hz, 1H); 6.75 (d, ³J(H,H) = 7.3 Hz, 2H), 7.32 (s, benzene).

(4) Crystal data for (4•tmeda): [(C₈H₇OLi₃)(C₆H₁₆N₂)₄][C₆H₆]_{1.53}, *M* = 1143.82, triclinic, *P*1, *a* = 18.38(3) Å, *b* = 21.64(4) Å, *c* = 23.26(2) Å, α = 73.1(1)°, β = 70.9(1)°, γ = 68.5(1)°, *V* = 7980(22) Å³, *Z* = 4, *D*_{calc} = 0.952 Mg m⁻³, μ = 0.56 cm⁻¹. Data (19 561 unique reflections) were collected at -90 ± 2 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation using the ω - 2θ scan technique (2θ_{max} = 44.1°). The structure was solved by direct methods and refined by block-matrix least-squares refinement of *F*² to wR2 = 0.288 and *R*(*F*) = 0.096 for 12 950 reflections with *F* > 4σ(*F*), 1561 parameters, GOF = 1.09, nonhydrogens anisotropic, benzylic hydrogens located, remaining hydrogens calculated. Five pairs of rotationally disordered benzene molecules have been found in difference Fourier syntheses. Each pair of rotationally disordered benzenes does not have full occupation: the total occupation for each pair ranges from 0.45 to 0.75. Therefore, the crystal contains holes between the tetrameric aggregates which are only partially filled with benzene molecules (this accounts for the low calculated density). The site occupation factors have been chosen so as to obtain reasonable isotropic *U* values for the benzene carbons. A total of 3.05 benzene molecules, fixed to a hexagonal geometry, were placed in the asymmetric unit. NMR analysis predicts 2.8 molecules in the asymmetric unit (see ref 3).

Table 1. Selected Bond Distances (Å) and Angles (deg) for (4-tmeda)₄^a

distance	range	av	angle	range	av
Li1–O1	1.89(1)–1.91(1)	1.91(1)	O1–Li1–O1'	132.9(5)–135.1(5)	134.0(5)
Li1–O1'	1.90(1)–1.95(1)	1.93(1)	C7–Li1–C8	120.8(5)–123.7(5)	122.6(5)
Li1–C7	2.30(1)–2.34(1)	2.32(1)	C7–Li2–O1'	100.8(4)–102.7(4)	101.8(4)
Li1–C8	2.27(1)–2.31(1)	2.29(1)	N1–Li2–N2	81.9(4)–85.1(4)	84.1(4)
Li2–O1'	1.93(1)–1.95(1)	1.94(1)	C8–Li3– π_{center}	167.2(5)–171.1(5)	169.1(5)
Li2–C7	2.27(1)–2.30(1)	2.29(1)	Li1–C7–Li2	68.2(4)–69.4(4)	68.7(4)
Li2–N1	2.21(1)–2.30(1)	2.25(1)	Li1''–C8–Li3	88.7(4)–90.4(4)	89.5(4)
Li2–N2	2.11(1)–2.15(1)	2.13(1)			
Li3–C8	2.07(1)–2.11(1)	2.09(1)			

^a The range and the average of the eight values in the two independent tetramers are given.

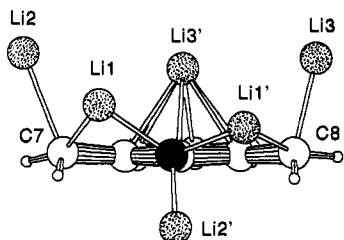


Figure 3. Partial structure showing the lithium coordination around each triple anion and the average positions of the benzylic hydrogens (view along the aryl ring plane).

ization results in a tub-shaped eight-membered ring of alternating O[−] and Li⁺ atoms (average O–Li, 1.92(1) Å). In this ring, the coordination sphere of the Li cations (Li1) is completed by bonding with the benzylic CH₂[−] groups (average C–Li, 2.31(1) Å). All Li cations in the (OLi)₄ ring possess similar coordination geometries.

The second type of lithium, Li2, bridges between one of the benzylic carbanions (C7, average C–Li, 2.29(1) Å) and an O[−] (average O–Li, 1.94(1) Å). Its coordination sphere is completed by a tmeda ligand that chelates Li with a long N–Li bond (average long N–Li, 2.25(1) Å) and a shorter one (average shorter N–Li, 2.13(1) Å). These differences are probably determined by different steric environments.

The third type of lithium, Li3, bridges one of the benzylic carbanions (C8) and the π -system of another aryl moiety within the tetramer. The CH₂–Li3 bond distance is short (average, 2.09(1) Å) but is in the range normally observed for a low (2 or 3)-coordinate lithium environment.^{5,6} The Li–C π -interactions range from 2.22(1) to 2.42(1) Å, with shorter contacts to C3 and C4 (average, 2.24(1) and 2.25(1) Å, respectively) and longer contacts to C6 (average, 2.40(1) Å). The average Li–C π -interaction of 2.32(1) Å is similar to that observed in structures of unsolvated lithium aryls.^{5,6}

All benzylic hydrogens were located in the difference Fourier map during the final stages of refinement. Normally the variance in hydrogen positions is large, but the close resemblance between the two tetramers and their units repeated by near S₄ symmetry permits obtaining relatively reliable average positions for the benzylic hydrogens. The benzylic carbons, C7 and C8, are both highly pyramidalized (see Figure 3). The average HCH angles for C7 and C8 are 110° and 108°, respectively. The sum of CCH and HCH angles is 336(1)° for C7 and 334° for C8 (for a planar sp² hybrid, the sum of bond angles should be 360°; for an ideal pyramidal sp³ hybrid this should be 328.6°). Benzylic alkali metal complexes generally show planar sp² benzylic groups bridging two alkali metals in a S₂ backside manner.⁷ However, in the current structure, both benzylic “sp³ lone pairs” are effectively localized and bridge

asymmetrically between two Li cations in a fashion comparable to a frontside S_{E2} substitution.

Crystals of 4-tmeda are only slightly soluble in toluene-*d*₈ at room temperature. A ⁷Li NMR (155 Mhz) spectrum shows three different Li signals with δ 2.48, 0.22 and −4.37 ppm (relative to 1 M LiBr/THF). The high-field signal probably arises from Li3, which is positioned in the aryl shielding cone.⁸ The ¹H NMR spectrum shows two different signals for the benzylic CH₂ groups and two different doublets for the aromatic protons attached to C3 and C5 (see NMR data).³ This indicates that the structure of the tetrameric aggregate is retained in solution. Heating the sample to +80 °C results in coalescence of the two aromatic doublets, while the triplet assigned to the proton attached to C4 remains sharp ($\Delta G^\ddagger = 17.5$ kcal/mol), indicating that the tetrameric structure is not stable at these temperatures. A ¹H NMR spectrum measured in THF-*d*₈ shows one broad singlet for both benzylic groups and one doublet for the protons attached to C4 and C5, indicating a species 4 which on the NMR time scale is symmetrical along its C–O axis.

The facile polyolithiation of 2,6-dimethylphenol contradicts the common idea that a deactivation is expected as soon the first benzylic proton has been removed. The activation energies for deprotonating the first and second methyl groups in lithium 2,6-dimethylphenoxide appear to be of comparable magnitude.⁹ A report that benzylic dilithiation of *p*- and *o*-xylene is slower than that of *m*-xylene suggests the idea that charge delocalization on only one set of alternant carbons (charge alternation) is preferred for a uniform distribution of charge in the π -system.¹⁰

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Supplementary Material Available: Crystallographic details, positional parameters, bond lengths, bond angles, anisotropic displacement parameters and positional parameters, for the hydrogen atoms (58 pages); final observed and calculated structure factors (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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