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THE CRYSTAL STRUCTURE OF THE REACTION PRODUCT OF n-BUTYLLITHIUM WITH 7,8-BENZOQUINOLINE

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Dedicated to Professor E.C. Taylor on the occasion of his 65th birthday.

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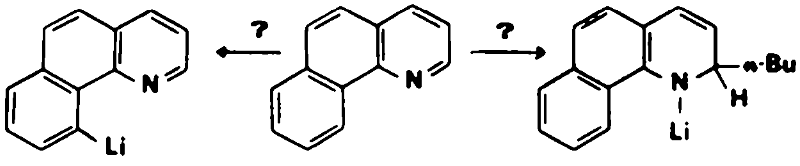
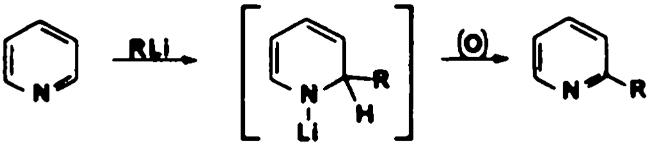
1-Lithio-2-n-butyl-2-hydro-7,8-benzoquinoline monoetherate (4), rather than a metallation product, is formed by the reaction of n-butyllithium with 7,8-benzoquinoline. The crystal and molecular structure has been determined from a single-crystal X-ray study. The compound crystallizes as a dimer in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions a = 11.518(2), b = 8.435(2), c = 19.339(4) Å, and β = 98.95(1)° Block-matrix least-squares refinement using 2806 unique reflections in the range $2° < \Theta < 33°$ and $I > 5\sigma(I)$ converged at R = 0.099 and R_w 0.094. The lithiums bridge the two nitrogen atoms to give planar four-membered ring

This paper is concerned with the nature of the reaction product of n-butyllithium with 7,8-benzoquinoline: does substitution (1) or does addition (2) occur?



1 2

Both these reaction courses are well precedented. One of the most convenient methods of preparing 2-substituted pyridine derivatives involves 1,2-addition of organolithium compounds. Indeed, the reactions of alkyl- or aryllithium reagents with pyridines,[2] quinolines,[3] bipyridines,[4,5] or 1,10-phenanthrolines,[5,6] have been shown to involve 1,2-addition to give intermediate 1,2-dihydropyridine derivatives. For example, the formation of the parent lithium amide, 3, has been demonstrated by NMR analysis of the reaction mixture of pyridine with n-butyllithium[7] or with phenyllithium.[8] On this basis, the addition product, 2 would be expected from the reaction of 7,8-benzoquinoline. However, solid state structures of intermediates such as 2 or 3 have not been determined previously.



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Addition, although well precedented by the examples discussed above, is by no means the only reaction possible. It also is well established that many substituents on a phenyl or aryl ring will activate an ortho or adjacent position towards metallation and that numerous heterocycles are known to undergo H/Li exchange with butyllithium.[9] These reactions are believed to occur by prior coordination of the substrate to the lithiation reagent, followed by metallation at a nearby position. Thus, 7,8-benzoquinoline might undergo lithiation to give 1, which also is expected to exhibit special stabilization due to N-Li chelation. However, at least under the conditions investigated initially (reaction with one mole of n-butyllithium in diethyl ether), this metal-hydrogen exchange did not compete with the addition, and 2 was the product actually obtained.

Because of our interest in helping to develop a detailed understanding of organolithium chemistry,[10] we have determined the X-ray structures of a number of organolithium compounds.[11,12] Since the publication of our review,[12] the crystallographic analysis of numerous additional amidolithium derivatives have been reported, especially by Lappert,[13] Snaith[14] and their groups. These reveal a rich variety of possible forms.[11d,12-16] Dimers, cyclic trimers and tetramers, as well as monomers and more complicated oligomers are now found in the expanding collection of amidolithium structural types.[11d,12-16]

Single-crystal X-ray structure determination shows that 2 exists as dimer 4, 1-lithio-2-*n*-butyl-2-hydro-7,8-benzoquinoline etherate, with two lithium atoms bridging the two nitrogen atoms of the benzoquinoline moieties (see stereoview, Fig. 1). Each lithium atom is further coordinated to an ether solvent molecule. Such double bridging arrangements have been observed previously, and are the preferred geometry for dimeric organolithium compounds.[11-14] The N(Li$_2$)N ring is approximately perpendicular to the polycyclic organic moiety. Theoretical calculations on the simplest cyclic models, (LiNH$_2$)$_n$ [n=2-4,6][16], have shown that this preference for perpendicular conformations is the consequence of largely ionic interactions of the Li$^+$'s with the roughly tetrahedrally oriented localized lone pairs on nitrogen.

As is apparent from Fig. 1, the relatively bulky diethyl ether ligand and the organic moiety in 4 limit the degree of aggregation to the dimer. Some of the geometrical parameters for 4 are given in Fig. 2.[17] The two slightly different Li-N (2.038(3) and 2.104(2) Å) and the Li-O (1.953(3) Å) bond lengths, as well as the Li-N-Li (77.6(1)°) and N-Li-N (102.4(1)°) bond angles are in the ranges exhibited by other dimeric lithium amides (i.e., Li-N, 1.98-2.16 Å; Li-O, 1.85-2.01 Å; Li-N-Li, 74.8-79.2°; N-Li-N, 102.2-105.2°).[11d,12,13c,14] Each lithium atom has an almost trigonal planar coordination of the three donor atoms (N, N', O). The crystallographic inversion center requires N, N', O, and O' to be coplanar, and the lithium atoms lie very close (0.05 Å) to this plane as well.

It is likely that metallation of 7,8-benzoquinoline (e.g., to give 1) can be activated under other conditions. The results of further experiments will be reported subsequently.

Experimental Section

Preparation of 1-lithio-2-*n*-butyl-2-hydro-7,8-benzoquinoline Monoetherate. A 1.6 *M* solution of *n*-butyllithium in hexane (1.5 ml, 2.4 mmol; EGA Chemie) under argon atmosphere was added to a rapidly stirred solution of 7,8-benzoquinoline (438 mg, 2.44 mmol; Janssen Chimica, sublimed prior to use) in anhydrous diethyl ether (30 ml). The ruby-red reaction mixture was stirred for one hour at room temperature and the volume reduced to about 15 ml under reduced pressure. The reaction mixture was cooled very slowly in a cryostat, over a period of five days, to -90°. The yellow crystals which had formed were filtered under argon and washed with anhydrous hexane at -90°C to give 581 mg (75.0% yield) of 2 as a yellow crystalline solid suitable for X-ray diffraction: ^{1}H-NMR (60 MHz, C$_6$D$_6$), σ 0.5-1.5 (*m*, 10 H, *n*-Bu), 0.72 (*t*, *J* = 7.0 Hz, 6 H, OCH$_2$CH$_3$), 2.97 (*q*, *J* = 7.0 Hz, 4 H, O$\underline{\mathrm{CH}_2}CH_3$), 4.10 (*m*, 1 H, vinylic), 5.50 (*m*, 1 H, vinylic), 6.49-7.63 (*m*, 6 H, aromatic).

X-Ray Crystallographic Study of 2. **Crystal Data:** Monomer = C$_{21}$H$_{28}$NOLi, *M* = 317.44, monoclinic space group *P*2$_1$/*c*, *a* = 11.518(2), *b* = 8.435(2), *c* = 19.339(4) Å, β = 98.95(1)°, *V* = 1856 Å^3, *Z* = 4, *D*$_{calc}$ = 1.136 g/cm^3 (at 117 K) with one monomer per asymmetric unit. Graphite monochromated Mo-Kα radiation, λ = 0.71069 Å.

A crystal of dimensions 0.5 x 0.3 x 0.1 mm was sealed in a glass capillary under argon. The crystal length was somewhat too large with respect to the monochromated beam causing systematic errors in the measurements. This was obvious from the large deviations of symmetry-related reflections from their average intensities. The ω-2Θ step scan data collection method, over the range $2° < \Theta < 33°$, was used to collect the data at 117° K. A total of 68612 reflection profiles were collected and averaged to give a unique set of 6973 data of which 2806 with $I > 5\sigma(I)$ were used in the calculations. The structure was solved by the direct methods program MULTAN[18]; 469 variables including all hydrogen parameters were refined anisotropically by block-matrix least-squares techniques[19] based on F^2 and weights $1/\sigma^2$ (F^2) to final error indices of *R* (F^2) = 0.099, *R*$_w$ (F^2) = 0.094, and R(F) = 0.070. The highest peak in the final F$_o$-F$_c$ synthesis was 0.49e/Å^3. Some of the hydrogen vibration parameters did not converge; except for these the shift/error ratio in the final refinement was less than 0.1.

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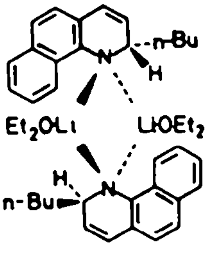

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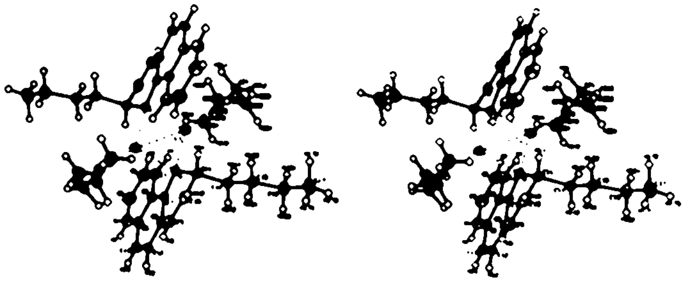

Figure 1. Stereoplot[20] of 4 at 117K; 50% probability ellipsoids. Note that the space around the central $N(Li_2)N$ ring is effectively filled by the diethyl ether ligands, the naphthalene moieties, and the n-butyl group.

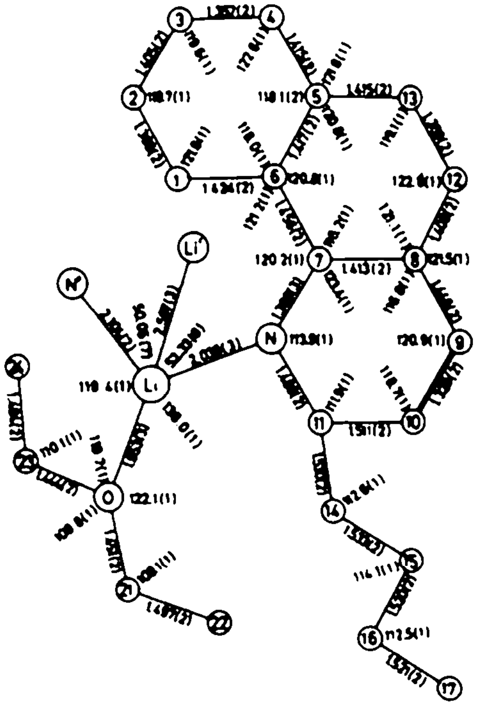

Figure 2. Structural parameters and labelling scheme for 4.