Figure 1. (A) Reaction of isolated NiC_{60}^+ with C_{60} background. (B) Isolated $Ni(C_{60})_2^+$. Absolute abundance is an arbitrary measure of FTMS signal intensity.

resonance ejection[9] of the less abundant isotopes, (3) subsequent sequential reactions of $^{58}Ni^+$ by direct attachment with preformed C_{60} heated off a solids probe at 350 °C to generate $^{58}NiC_{60}^+$ (m/z 778) and, following its isolation, then $Ni(C_{60})_2^+$ (m/z 1498) (Figure 1A), and (4) isolation of the $^{58}Ni(C_{60})_2^+$ by double resonance ejection (Figure 1B). Unfortunately, under these conditions the remaining signal intensity was not sufficient to obtain unambiguous collision-induced dissociation data.[10]

The results reported here suggest the possibility of a stable family of bis-fullerene "dumbbell" complexes in analogy to the bis-benzene and metallocene compounds. While only the bis-C_{60} nickel complex has been observed to date, variation of the experimental conditions will undoubtedly yield additional members of the bis-fullerene family (other metals and other fullerenes). Furthermore, we are also currently attempting to synthesize macroscopic amounts of these interesting and potentially useful complexes in our laboratory.[11]

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(11) Preliminary results suggest that we may have successfully synthesized $Fe(C_{60})_2$ in solution, and we are currently characterizing it.

Crystal Structure of Lithium Diisopropylamide (LDA): An Infinite Helical Arrangement Composed of Near-Linear N-Li-N Units with Four Units per Turn of Helix

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Although the number of crystal structure reports of organic lithium derivatives has mushroomed over the past decade or so,[1] a report of the most important lithium reagent, indeed, one of the most utilized reagents throughout organic synthesis, lithium diisopropylamide (LDA), has been conspicuously absent. A combination of low nucleophilicity and high kinetic basicity makes this hindered amide invaluable in proton abstraction applications.[2] Collum and Galiano-Roth recently discussed[3] the scarce structural information that is available on LDA systems in their account of the (LDA·tetrahydrofuran)$_2$[4] solution dimer established by ^6Li and ^{15}N NMR spectroscopic studies. The problem is that although LDA does have some solubility in hydrocarbon solvents, it tends to readily precipitate when prepared in them. Dissolution can be effected by addition of the donor tetrahydrofuran although its concentration and the solution temperature must be carefully controlled to minimize solvent degradation.[5] Described herein is a simple procedure involving the donor TMEDA (tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$),[6] which yields a *crystalline* form of LDA showing no complexation. Once isolated from solution, the crystals retain their integrity under a protective inert atmosphere, and their quality is such that we have successfully determined the crystal structure by an X-ray diffraction study. This confirms that uncomplexed LDA is a polymer,[7] but the nature of the infinite association is unprecedented with near-linear N-Li-N units in a helical assembly.

The crystalline composition can be prepared in the following way. Commercial samples (10-mmol scale) of *n*-butyllithium (or *tert*-butyllithium) and diisopropylamine mixed together in hexane at 295 K under an argon blanket afford the conventional LDA precipitate, to which is added TMEDA (20 mmol). Complete dissolution is achieved by gently warming the stirred mixture. Gradual cooling to ambient temperature deposits from the solution

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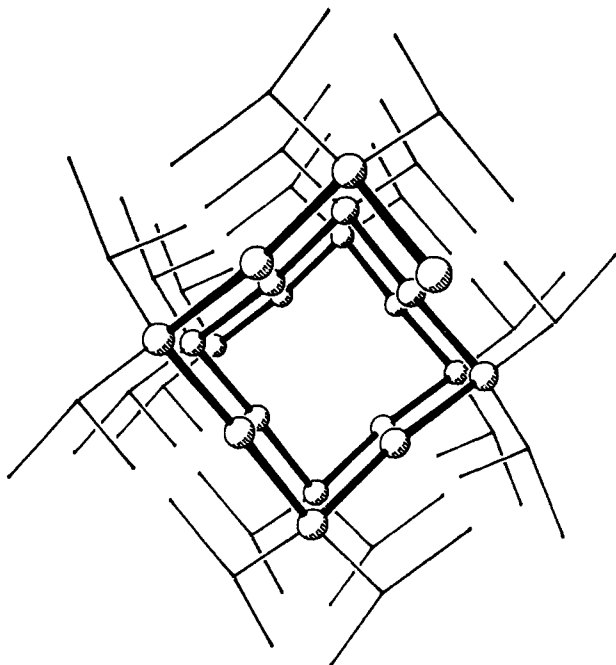
Figure 1. An axial view of the helix structure of crystalline LDA. Hydrogen atoms have been omitted for clarity.
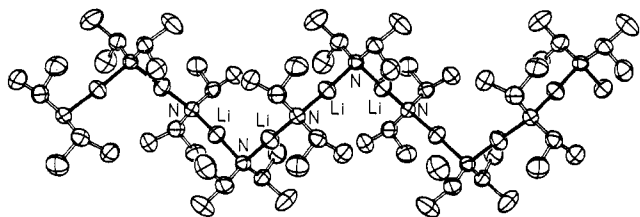

Figure 2. A side view of the same section of the helix showing thermal ellipsoids (at the 50% probability level). A representative sample of N and Li atoms are labeled.

Table I. Selected Bond Lengths (Å) and Angles (deg)

Li(1)-N(1)	1.957 (5)	N(1)-Li(1)-N(2')	177.9 (3)
Li(1)-N(2')	1.934 (5)	N(1)-Li(2)-N(2)	174.1 (2)
Li(2)-N(2)	1.956 (4)	Li(1)-N(1)-Li(2)	108.3 (2)
Li(2)-N(1)	1.939 (4)	Li(1')-N(2)-Li(2)	109.5 (2)

a crop of almost colorless (with slight brown tinge) crystals.[8] Removing the mother liquor, washing with hexane aliquots, and evacuating to dryness has no adverse effect on their crystallinity, and although sensitive to atmospheric moisture and oxygen they are nonpyrophoric. Traces of diisopropylamine and, less significantly, of TMEDA in the crystalline composition can be detected by ^{1}H NMR spectroscopic analysis.[9] Based on integration ratios, a typical empirical formula is [(Pr$^i_2$NLi)(Pr$^i_2$NH)$_{1/10}$(TMEDA)$_{1/40}$].

Pure LDA is a fine powdery white solid, so its crystalline state here must be promoted by the small quantities of Pr$^i_2$NH/TMEDA present. However, these potential donor ligands do not show up in the electron density map obtained by the X-ray dif-

fraction study. They form no part of the regular crystalline structure; possibly they play a role in polymer chain termination at the crystal surface and at defect sites in the structure.

LDA adopts an eye-catching helical arrangement (Figure 1) in the crystal phase.[10] An alternative view looking through a section of the helix shell, rather than through its central cavity, is shown in Figure 2. Table I lists selected bond lengths and bond angles. Each two-coordinate Li$^+$ center engages in one short bond (average length, 1.937 Å) and one slightly longer bond (average length, 1.957 Å) to essentially tetrahedral, four-coordinate N$^-$ centers. The polymer is thus composed of unsymmetrical N-Li-N units, approximately linear in shape (average N-Li-N bond angle, 176°). These triatomic units link up so that the short and long N-Li bonds alternate throughout the coiled structure. A turn of the helix consists of four such units (eight N-Li bonds in total). The repeat distance between turns (i.e., between like atoms that are eclipsed along the axis of the helix) is 9.567 Å. Finally, it should be pointed out that the centrosymmetric crystal structure contains equal numbers of right-handed and left-handed helices. Figure 1 depicts the latter type.

(8) Yield of first batch obtained after 24 h of refrigerator cooling, 59% (based on consumption of freshly standardized Bu^{t}Li). Attempts to optimize the yield are in progress. This crystalline form of LDA is the subject of a preliminary patent filed by the Associated Octel Co. Ltd., Ellesmere Port, U.K.

(9) ^{1}H NMR spectrum (recorded at 400 MHz in tetrahydrofuran-d_8 solution; 263 K): Pr^i(CH), 1 H, sep, δ 2.99 ppm; Pr^i(CH)-amine, ≪1 H, oct, δ 2.85 ppm; CH$_2$-TMEDA, ≪1 H, s, δ 2.29 ppm; CH$_3$-TMEDA, ≪1 H, s, δ 2.14 ppm; Pr^i(CH$_3$), 6 H, d, δ 0.97 ppm; Pr^i(CH$_3$)-amine, <1 H, d, δ 0.94 ppm. Relative to TMS, δ 0.00 ppm. A comparison with a solution of Pr$^i_2$NH and TMEDA in the same solvent indicates that both ligands are "free" here and not attached to the Li$^+$ cations. In this medium the Li$^+$ centers will be complexed by tetrahydrofuran molecules (see ref 3 for details).

(10) Crystal data: C$_6$H$_{14}$NLi, M = 107.1, monoclinic, $P2_1/n$, a = 9.146 (3) Å, b = 9.567 (3) Å, c = 17.740 (7) Å, β = 92.91 (3)°, V = 1550.4 Å^3, Z = 8, D_{calcd} = 0.918 g cm^{-3}, λ(Cu Kα) = 1.541 84 Å, μ = 0.354 mm^{-1}, $F(000)$ = 480. Measurements were made at 240 K on a Stoe-Siemens diffractometer with an Oxford Cryostream cooler from a crystal of size 0.50 × 0.58 × 0.61 mm; 1880 unique observed reflections were used for structure determination by direct methods and least-squares refinement on F, with weighting w = $1/\sigma^2(F)$. H atoms were constrained, and other atoms were assigned anisotropic thermal parameters. At convergence, R = 0.0562, R' = 0.0673, goodness of fit = 1.01 for 170 parameters. All features in a final difference synthesis were within ±0.18 e Å^{-3}. Program system: SHELXTL (G. M. Sheldrick, University of Göttingen, Germany).

Novel Class of Asymmetric Zwitterionic Rotaxanes Based on α-Cyclodextrin

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Rotaxanes[1] are molecules in which a cyclic structure is threaded by a chain or other linear subunit having bulky ends that prevent the dissociation (or unthreading) of the cyclic and linear components. We report here the synthesis of a new class of rotaxanes based on the inclusion of alkyl chains by α-cyclodextrin (α-CD). The CD is locked onto the alkyl chain by two different bulky groups covalently attached to the ends of the chain. Two isomeric rotaxanes are formed which differ by the orientation of the CD torus with respect to the terminal groups.

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