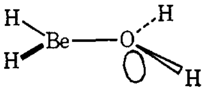
and CsF_2^+[24] has been published, LiF_2^- and LiF_2^+ are of interest.

(3) In line with studying the donor–acceptor and internal rotation aspects of H_3NBH_3, a complete study of H_2OBeH_2 is logically the next step. While this system is isoelectronic to ethylene, there exists another reasonable geometry with its rotamers



(4) There is still considerable disagreement on the structure of the Grignard reagent (RMgX·etherate). The following isomorphic replacement should not alter the characteristics of the Grignard reagent as a donor–acceptor complex: H for R, Be for Mg, F for X (Cl, Br, I), H_2O for an ether.

(5) The simple triatomic system involving H, Be, and F is of interest. HBeF is isoelectronic to HCN. The isomer BeHF is reasonable as this is a normal donor–acceptor complex. HFBe should be considered by analogy to the Ar–HCl gas interaction,[25] where the observed structure is ArClH.

(6) Li_2F^+ appears to be a highly bound cation, which by analogy to Li_2O[10] is probably linear. It therefore seems reasonable that at least one crystalline phase of mixed crystal LiF·LiX should have the structure $Li_2F^+X^-$. This would be facilitated by a large and noncomplexing anion X such as SbF_6^-, as crystal packing favors equally sized ions.

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(24) As pointed out in ref 23, CsF_2^+ is isolectronic to XeF_2. Therefore LiF_2^+ offers an interesting contrast with the previously studied HeF_2 (L. C. Allen, R. M. Erdahl, and J. L. Whitten, *J. Amer. Chem. Soc.*, 87, 3769 (1965)) and HF_2^- (R. M. Erdahl, see ref 15).

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π Complexation in Ion Pair Bonding. The Structure of Benzyllithium Triethylenediamine[1]

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Abstract: The crystal structure of benzyllithium triethylenediamine, $C_6H_5CH_2^-Li^+N(C_2H_4)_3N$, has been determined from three-dimensional X-ray data collected by counter methods. A full-matrix least-squares refinement on 714 reflections resulted in a final unweighted discrepancy factor of 7.9%. The material crystallizes in the orthorhombic space group $P2_12_12_1$ in a cell of dimensions $a = 16.231\,(8)$, $b = 6.255\,(3)$, $c = 11.800\,(6)$ Å. The measured and calculated densities are 1.17 and 1.16 g/cm³, respectively. The structure consists of infinite polymeric chains of solvated ion pairs linked by triethylenediamine cages which propagate along the *c* direction. Each ion pair molecule consists of a benzyl carbanion and two half triethylenediamine cages coordinated to a lithium cation. The average C–C distance in the carbanion is 1.40 (1) Å and the average Li–N distance is 2.10 (1) Å. Each lithium atom is formally sp^2 hybridized if the point on the carbanion which is closest (2.17 Å) to the lithium atom is considered as a coordination site. Evidence is presented for complexation of the lithium cation with the π cloud of the benzyl carbanion. A discussion of the bonding is presented.

The lack of structural knowledge of organolithium compounds is in sharp contrast to their widespread use.[2] The only detailed crystallographic structural investigations have been of unsolvated CH_3Li,[3a] C_2H_5Li,[3b] and $LiAl(C_2H_5)_4$.[4] In these and other alkyllithium compounds,[5] polynuclear species are formed which have structural properties which suggest electron deficient bonding similar to that found in organoaluminum, -beryllium, and -magnesium compounds.

Addition of Lewis bases greatly enhances the reactivity of organolithium reagents in metalation, substitution, and polymerization reactions. Examples are the telomerization process,[6] where stable aryl-lithium–amine adduct intermediates give rise to high molecular weight "telomers," and rapid metalations of previously unreactive hydrocarbons by *n*-butyllithium activated by 1,4-diazabicyclo[2.2.2]octane (triethylenediamine) or N,N,-N′,N′-tetramethylethylenediamine.[7,8] Eberhardt and Butte[6] have postulated that the amine decreases the polarizing power of the lithium moiety, thus weakening the covalent nature of the carbon–lithium bond. This

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(1) This work was supported by the Advanced Research Projects Agency under Contract SD-131 and the National Science Foundation.

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results in a reactive carbanion bonded to a lithium cation by ion pair forces. Hückel and self-consistent field molecular orbital calculations substantiate the agreement between the predicted electronic absorption spectra of the benzyl carbanion and the measured spectrum for benzyllithium in tetrahydrofuran.[9] Although small bathochromic shifts as a function of counterion size have been observed in related systems, the principal interaction of the cation has been suggested to be mainly ionic.[10] However, in the closely related fluorenyllithium system, direct evidence from nuclear magnetic resonance[11] and kinetic measurements[12] has suggested strong interactions between the fluorenyl carbanion's π cloud and the lithium cation. In order to clarify the nature of bonding and solvating forces in organolithium compounds, the single crystal structural analysis of benzyllithium triethylenediamine was undertaken.

Experimental Section

Toluene (Fisher Scientific Co.) and hexane (Fisher Spectroanalyzed) were dried over sodium wire and degassed with argon prior to use. *n*-Butyllithium in hexane was obtained from Foote Mineral Co., and used without further purification. Triethylenediamine (Houdry Process Corporation) was purified by sublimation at 0.1 mm and 28° in an argon atmosphere. All chemical reactions were performed in an argon atmosphere drybox which continually recycled the atmosphere to remove traces of air and water.[13]

Crystals of $C_6H_5CH_2LiN(C_2H_4)_3N$ were first prepared by the method of Eberhardt and Butte,[6] but only microcrystalline powders were obtained. By addition of 2.5 ml of 1.6 *M* *n*-butyllithium (0.004 mole) to a solution of 0.44 g of triethylenediamine (0.004 mole) in 20 ml of hexane and 10 ml of toluene at 23°, a straw-colored solution was formed which gradually turned bright yellow over a 1-hr period. After 72 hr, the solution decolorized, leaving a crop of bright yellow crystals. A typical reaction yielded 0.77 g (79.7%) of benzyllithium triethylenediamine. The compound is insoluble in benzene, toluene, hexane, and diethyl ether, extremely pyrophoric in air, and decomposes under argon at 140–165° in a sealed tube. *Anal.* Calcd for $C_{13}H_{19}LiN_2$: C, 74.31; H, 9.05; Li, 3.31; N, 13.34. Found: C, 74.15; H, 9.15; Li, 3.27; N, 13.07.

The electronic absorption spectrum was recorded on a Cary Model 14RI spectrophotometer. Deoxygenated Nujol mulls of crystalline material were prepared and mounted on quartz plates in the drybox. No sample decomposition was noticeable after 24 hr.

Collection and Reduction of the Intensity Data

An optical study indicated that the crystals were biaxial and monochroic. Crystals were placed inside 0.2-, 0.3-, and 0.5-mm capillaries which were sealed first with wax in the drybox, and later by using a torch in the air. Systematic absences as determined from precession and Weissenberg photographs (Mo Kα, λ 0.7107 Å; $t = 23°$) were: $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$. These absences are uniquely consistent with the orthorhombic space group $P2_12_12_1$ ($D_2{}^4$).

The crystal selected for further study was a bright yellow parallelepiped with the well-developed [100] and [010] faces mounted parallel to the capillary wall; dimensions were 0.15 × 0.35 × 0.48 mm. The [001] direction was nearly coincident with the ϕ axis of a four-circle manual Picker diffractometer. Lattice constants and standard deviations (given in parentheses) obtained from the least-squares refinement of the $(\sin\theta/\lambda)^2$ values of 12 carefully centered high angle reflections[14] are: $a = 16.231$ (8); $b = 6.255$ (3); $c = 11.800$ (6); $V = 1197.93$ Å^3 (Cu Kα_1, λ 1.54051 Å, 23°). The calculated density of 1.16 g/cm^3 for four molecules of $C_6H_5CH_2LiN(C_2H_4)_3N$ per unit cell agrees well with the observed density of 1.17 g/cm^3 measured by flotation in a mixture of hexane, benzene, and bromobenzene. With four molecules/unit cell, $P2_12_12_1$ requires all atoms to be in general positions.

X-Ray intensity measurements were made with Cu Kα radiation. The peak width was estimated by narrow source–open counter ω scans of several reflections; the width of a peak at half-height was 0.24°. The intensities were measured using a takeoff angle of 1.0° (75% of the maximum intensity as a function of takeoff angle) and a scintillation counter mounted 21 cm from the crystal. Data were collected up to $2\theta_{\max} = 99°$ by the θ–2θ scan technique using a constant scan rate of 1°/min. All reflection positions were calculated from B-101 using the twelve centered reflections mentioned above.[12] For the intervals $2\theta < 20°$, $20° \leq 2\theta < 35°$, $35° \leq 2\theta < 85°$, $85° \geq 2\theta$, scans of 50, 60, 65, and 70 sec with offsets of 0.4, 0.5, 0.6, and 0.6°, respectively, were used. Stationary background counts of 20 sec were taken at the beginning and end of each scan. The diffracted beam was passed through a 1.0-mm collimator and filtered with a 0.0005-in. nickel foil. No additional attenuation was supplied since the response of the counter was linear in the range of intensities which were measured.

A strip chart recorder was constantly monitored to check centering, peak shape, and overlap. The pulse height analyzer was set at an 85% window centered on a Cu Kα_1 peak. To check for crystal decomposition, a standard peak was monitored every 6 hr during the course of data collection. No decomposition of the sample or systematic variation of the intensity was observed.

A total of 728 independent reflections were recorded for each of two symmetry related forms, hkl and $\bar{h}\bar{k}\bar{l}$. The intensities were corrected for background and Lorentz-polarization effects.[15] The linear absorption coefficient $\mu = 5.14$ cm^{-1} suggested that the effects of absorption would be negligible. A survey of transmission factors indicated a variation of only 3%; therefore, no absorption correction was applied. Unobserved reflections ($I_\sigma < 3\sigma(I)$) were given a raw intensity of $\sigma(I)$.[16,17] The two symmetry related forms of data were then averaged to give 714 independent reflections, 14 being rejected on the basis of seriously conflicting intensities between symmetry related pairs. The resulting 714 reflections had an agreement factor $R = 0.046$, where R is defined as $\Sigma F_{av}/\Sigma|\Delta F_{av}|$ with

$$\begin{aligned} F_{av} &= (F_{hkl} + F_{\bar{h}\bar{k}\bar{l}})/2 \\ |\Delta F_{av}| &= |(F_{hkl} - F_{\bar{h}\bar{k}\bar{l}}|/2 \end{aligned} \qquad (1)$$

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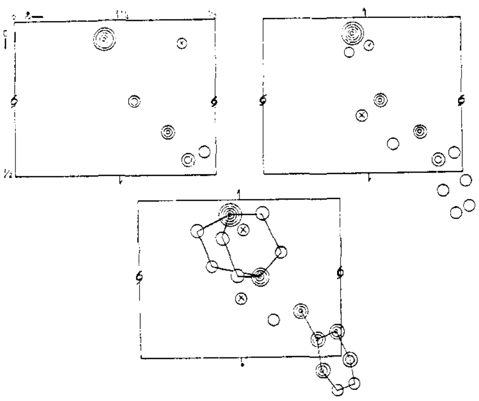

Figure 1. Appearance of E maps after each cycle of the partial tangent formula. Spurious peaks are denoted by ×.

A Wilson plot was first used to put the data on an absolute scale.[18] A large spread in the number of points was observed with a rather low temperature factor of $B = 2.71$ Å^{-2}. This method assumes that the temperature correction to the atomic scattering factors has the Gaussian form $e^{-B\sin^2\theta/\lambda^2}$ where B is the overall temperature factor. A much more general temperature behavior is assumed by the K curve method and this was used to simultaneously correct for thermal motion and data scaling.[19] Normalized structure factor amplitudes $E_{\vec{h}}$ were calculated, and statistical tests were applied to confirm the choice of noncentrosymmetric space group. Results appear in Table I.

Table I. Statistical Test Results for $C_6H_5CH_2^-Li^+N(C_2H_4)_2N$[a]

Quantity	Calculated	Theoretical Centric	Theoretical Accentric
$\langle E\rangle_{av}$	0.887,[b] 0.877	0.798	0.886
$\langle E^2\rangle_{av}$	1.00, 1.00	1.00	1.00
$\langle E^2 - 1\rangle_{av}$	0.773, 0.806	0.968	0.736
% >1	31.62, 31.07	32.00	37.00
% >2	3.03, 3.32	5.00	1.80
% >3	0.23, 0.31	0.30	0.01

[a] "K-Curve," Program for the Generation of Normalized E's for the IBM 360, S. Patterman, University of Illinois, 1969. [b] Statistics excluding all 0 level reflections.

Solution and Refinement

Phase Determination. A Σ-2 listing of all interacting reflections with $|E_h| \geq 1.5$ was obtained and three two-dimensional phases were assigned to specify the origin.[20] The formula for starting a symbolic phase determination[21] in a noncentrosymmetric space group[22] is given by eq 2, where $\phi_{\vec{h}}$ is the phase associated with $|E_{\vec{h}}|$.

$$\phi_h = \langle \phi_{\vec{k}} + \phi_{(\vec{h}-\vec{k})}\rangle_{\vec{k}_r} \tag{2}$$

By the use of the Σ_1 formula for $P2_12_12_1$,[22] the probability of the sign of the $\vec{h} = 4, 0, 0$ reflection being positive was 97%, and the reflection was often used in checking assignments in the symbolic addition procedure. A total of three symbols were assigned and the phase of $\vec{h} = 8, 5, 0$ was given a value of 0 in order to specify the enantiomorph (Table II).[23] Interactions in (2) involving only two-dimensional reflections were avoided. A total of 37 reflections were assigned phases by hand; there were several indications that $p = -\pi/2$ but no definite indications for a and b. In $P2_12_12_1$, a and b can only have phases of 0 or π.[24] Four possible combinations ($a = 0, b = \pi$; $a = \pi, b = 0$; $a = 0, b = 0$; $a = \pi, b = \pi$) were expanded by the use of the tangent formula (eq 3) and E maps[25] computed for each. The map for $a = \pi$, $b = 0$ showed four relatively large peaks

$$\tan \phi_{\vec{h}} = \frac{\sum_{\vec{k}} |E_{\vec{k}}E_{\vec{h}-\vec{k}}| \sin(\phi_{\vec{k}} + \phi_{\vec{h}-\vec{k}})}{\sum_{\vec{k}} |E_{\vec{k}}E_{\vec{h}-\vec{k}}| \cos(\phi_{\vec{k}} + \phi_{\vec{h}-\vec{k}})} \tag{3}$$

which were used as a basis for a partial structure determination.[26] A new E map based on the tangent formula expansion of phases from the four atoms ($|E_{calcd}| > 0.25|E_{obsd}|$) showed thirteen peaks, two of which later proved to be incorrect, which were used for another expansion ($|E_{calcd}| \geq 0.50|E_{obsd}|$). The complete structure appeared in this last cycle along with two spurious peaks. Figure 1 shows the appearance of the structure at the various stages.

Table II. Phase Assignments

Reflection H	K	L	Phase	E
13	0	5	$+\pi/2$	3.13
1	1	0	$+\pi/2$	2.34
3	0	2	0	2.62
8	5	0	0	2.44
2	0	2	a	2.42
3	1	0	p	3.01
12	0	4	b	2.35

The structure was refined by full-matrix, least-squares techniques using a modified version of ORFLS.[27] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes; w, the weight, was set equal to unity. Agreement factors used in subsequent discussion are defined as

$$R_1 = (||F_o| - |F_c||)/\Sigma(|F_o|)$$

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$$

The atomic scattering factor tables of Hansen[28] were used for C, H, and N, while the values given in the International Tables[29] were used for Li$^+$.

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Table III. Atomic Positional and Thermal Parameters for All Nonhydrogen Atoms

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Li	0.3336 (8)[b]	0.8472 (24)	0.4108 (10)	0.0023 (5)	0.0237 (50)	0.0033 (10)	0.0025 (15)	0.0007 (7)	0.0014 (21)
C(15)	0.4148 (4)	0.5654 (14)	0.3921 (6)	0.0031 (3)	0.0330 (30)	0.0072 (7)	0.0027 (9)	−0.0012 (4)	−0.0028 (15)
C(1)	0.4639 (5)	0.6945 (14)	0.4607 (6)	0.0033 (3)	0.0276 (28)	0.0063 (8)	0.0027 (9)	0.0009 (5)	0.0012 (13)
C(2)	0.4914 (5)	0.9045 (16)	0.4276 (7)	0.0040 (4)	0.0388 (36)	0.0072 (8)	0.0001 (10)	0.0002 (5)	0.0032 (16)
C(3)	0.5350 (6)	0.0393 (16)	0.5004 (9)	0.0047 (4)	0.0325 (31)	0.0111 (9)	−0.0030 (12)	0.0008 (6)	−0.0006 (17)
C(4)	0.5535 (5)	0.9776 (19)	0.6086 (9)	0.0044 (4)	0.0455 (42)	0.0085 (9)	−0.0007 (12)	−0.0005 (5)	−0.0038 (19)
C(5)	0.5293 (5)	0.7819 (19)	0.6449 (7)	0.0034 (4)	0.0554 (45)	0.0054 (8)	0.0003 (12)	−0.0002 (5)	0.0008 (17)
C(6)	0.4854 (5)	0.6423 (15)	0.5746 (7)	0.0041 (4)	0.0319 (31)	0.0056 (7)	0.0031 (10)	0.0028 (5)	0.0033 (13)
N(7)	0.2292 (3)	0.0673 (11)	0.0588 (4)	0.0029 (3)	0.0314 (25)	0.0039 (5)	0.0007 (7)	0.0001 (3)	−0.0001 (9)
C(8)	0.3154 (5)	0.0059 (32)	0.0494 (7)	0.0035 (4)	0.1533 (103)	0.0060 (7)	0.0061 (21)	0.0003 (4)	0.0141 (27)
C(9)	0.3529 (5)	0.9749 (35)	0.1695 (7)	0.0034 (4)	0.1959 (131)	0.0065 (7)	0.0117 (22)	0.0015 (5)	0.0226 (32)
N(10)	0.2929 (3)	0.9736 (10)	0.2552 (5)	0.0026 (2)	0.0287 (22)	0.0050 (5)	0.0005 (7)	−0.0005 (3)	0.0004 (10)
C(11)	0.2576 (10)	0.1880 (20)	0.2555 (9)	0.0208 (14)	0.0518 (49)	0.0106 (1)	0.0216 (23)	−0.0107 (11)	−0.01168 (20)
C(12)	0.2253 (9)	0.2536 (18)	0.1344 (9)	0.0144 (10)	0.0390 (44)	0.0102 (10)	0.0068 (18)	−0.0079 (9)	−0.0007 (18)
C(13)	0.1848 (7)	0.8963 (17)	0.1125 (9)	0.0089 (7)	0.0434 (42)	0.0106 (10)	−0.0118 (14)	−0.0059 (7)	0.0070 (18)
C(14)	0.2275 (8)	0.8310 (20)	0.2250 (10)	0.01187 (9)	0.0618 (52)	0.0138 (12)	−0.0193 (18)	−0.0091 (9)	0.0194 (21)

[a] The form of the anisotropic thermal ellipsoid is given by $\exp-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] The numbers in parentheses represent standard deviations.

Three cycles of refinement on the scale, and positional and isotropic temperature factors for the 16 atoms located in the final E map (all observed and unobserved data), gave $R_1 = 0.20$. A difference Fourier map[30] revealed the presence of anisotropic thermal motion. Several small peaks (1-2 e/Å^3) appeared around the amine ring but at this stage of refinement were ignored. Four more cycles of refinement employing anisotropic temperature factors for all 16 atoms lowered R_1 to 12.5 and R_2 to 10.6. A difference map located all the benzyl ring protons with peaks of 0.6–0.8 e/Å^3 and showed only diffuse peaks, 0.2–0.5 e/Å^3, for the amine's protons. By using difference Fourier techniques, all 17 hydrogen atoms in the asymmetric unit were assigned and used in the further stages of refinement. The chemical reasonableness of these parameters was verified by using a computer program to calculate theoretical hydrogen atom coordinates assuming sp^3 and sp^2 hybridized carbon atoms.[31] Their positional and thermal parameters were not varied, and they were assigned temperature factors equal to those of the parent carbon atom at the convergence of isotropic refinement. Three more cycles of refinement including hydrogen atoms lowered R_1 to 0.079 and R_2 to 0.073. The error of observation of unit weight was 1.69. No systematic variation in a plot of $|F_o|$ $vs.$ $(|F_o| - |F_c|)^2$ was observed. The final agreement factors for all data are $R_1 = 0.079$, $R_2 = 0.073$; and $R_1 = 0.068$, $R_2 = 0.063$, excluding unobserved reflections. The lithium atom was refined as the cation and no attempt was made to refine neutral lithium atoms or to ascribe negative character to the benzyl ring. The positional and thermal parameters derived from the last least-squares cycle for all 16 nonhydrogen atoms in the asymmetric unit are given in Table III, and parameters for the hydrogen atoms in Table IV. A compilation of observed and calculated structure factors is included (Table V).

Table IV. Hydrogen Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å^2
C(15)H(1)	0.4083	0.6133	0.3083	4.17
C(15)H(2)	0.3666	0.4500	0.4166	3.89
C(2)H(1)	0.4907	0.9601	0.3427	4.86
C(3)H(1)	0.5436	0.2053	0.4658	4.73
C(4)H(1)	0.5806	0.0727	0.6640	4.03
C(5)H(1)	0.5341	0.7480	0.7256	2.89
C(6)H(1)	0.4755	0.5128	0.6034	2.08
C(8)H(1)	0.3185	0.8611	0.0097	7.01
C(8)H(2)	0.3456	0.0987	0.0039	7.01
C(9)H(1)	0.3901	0.0955	0.1848	7.41
C(9)H(2)	0.3860	0.8482	0.1765	7.41
C(11)H(1)	0.2926	0.2842	0.2872	9.67
C(11)H(2)	0.2067	0.1802	0.3043	9.67
C(12)H(1)	0.2658	0.3609	0.1065	6.83
C(12)H(2)	0.1743	0.3154	0.1357	6.83
C(13)H(1)	0.1276	0.9516	0.1333	5.37
C(13)H(2)	0.1752	0.7766	0.0671	5.37
C(14)H(1)	0.1873	0.8267	0.2893	8.80
C(14)H(2)	0.2481	0.6880	0.2193	8.80

[a] Thermal parameters of the parent carbon atom at the conclusion of isotropic refinement.

A final difference Fourier revealed many spurious peaks of 1.0–1.5 e/Å^3 in the vicinity of the carbon atoms of the triethylenediamine ring. As mentioned previously, several small peaks were noticed in the earlier stages of refinement but were ignored. The root mean square displacements along the principal temperature factor ellipsoids, Table VI, for carbon atoms C(8)–C(14) are very large in comparison to the rest of the structure. Some form of rotational disorder or rigid body rotation around the N(7)–N(10) axis is indicated by these displacements. A reevaluation of earlier Fourier maps indicates that a nonstatistical disorder (5:1) may be involved. In view of the limited amount of data in comparison to the large number of variables involved, no attempt was made to refine a disordered model. The effects of the disorder have probably been incorporated into the anisotropic thermal motion. Commonly made thermal corrections to bond distances and angles[32] are therefore not very meaningful in this case and are not reported.

Results and Discussion

The structure of benzyllithium triethylenediamine consists of infinite polymeric chains which are oriented along the 2_1 axes parallel to the c direction (Figure 2). The basic repeating unit contains a lithium cation, a

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(30) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "ERFRE-2, A Three Dimensional Crystallographic Fourier Summation Program," Massachusetts Institute of Technology, Cambridge, Mass., 1962.

(31) Program "Hygen," F. Ross and G. Stucky, University of Illinois, Urbana, Ill.

(32) W. R. Busing and H. A. Levy, *Acta Cryst.*, 17, 142 (1964).

Table V. Observed and Calculated Structure Factor Amplitudes in Electrons. Unobserved Reflections Are Indicated by an Asterisk

K	L	OBS	CAL
******H= 0********			
4	0	4.8	4.5
6	0	2.0	0.7*
1	1	66.1	66.4
2	1	15.0	16.8
4	1	3.2	2.7
5	1	3.5	1.8
6	1	4.9	3.0
0	2	23.3	21.7
1	2	69.9	67.2
2	2	23.6	24.0
3	2	14.1	16.2
4	2	8.0	8.2
5	2	2.0	1.6*
6	2	2.1	2.7*
1	3	7.4	7.1
2	3	9.9	8.8
3	3	7.5	7.9
4	3	13.2	12.8
5	3	8.2	7.6
0	4	13.9	14.3
1	4	9.8	10.8
2	4	5.2	5.1
3	4	16.5	15.5
4	4	5.8	4.7
5	4	1.9	2.6*
1	5	30.7	30.0
2	5	1.6	2.2*
3	5	10.8	11.6
4	5	2.0	2.6*
5	5	2.0	2.4*
0	6	41.6	43.1
1	6	3.8	3.3
2	6	13.5	12.3
3	6	4.8	4.7
4	6	9.6	8.9
5	6	4.9	5.0
1	7	3.8	3.4
2	7	12.1	12.9
3	7	23.9	24.1
4	7	1.9	2.2*
0	8	5.4	5.8
1	8	9.0	11.1
2	8	1.9	1.1*
3	8	7.7	7.6
4	8	8.0	8.8
1	9	10.7	10.6
2	9	8.9	7.2
3	9	5.7	5.6
0	10	14.6	15.5
1	10	3.6	3.8
2	10	1.9	1.7*
3	10	8.0	8.5
1	11	3.6	3.7
2	11	4.6	4.4
******H= 1********			
1	0	85.3	89.0
2	0	21.4	21.5
3	0	4.9	5.6
4	0	3.2	1.8
5	0	1.9	0.3*
6	0	2.0	1.8*
0	1	0.9	2.3*
1	1	15.1	14.4
2	1	18.7	18.3
3	1	24.3	24.6
4	1	6.7	6.4
5	1	2.9	2.0
6	1	1.9	1.2*
0	2	58.6	60.7
1	2	23.8	20.0
2	2	14.8	14.1
3	2	18.6	17.1
4	2	3.9	3.8
5	2	8.6	8.7
6	2	5.3	6.0
0	3	1.3	1.7*
1	3	10.2	8.7
2	3	19.2	19.8
3	3	14.3	13.1
4	3	8.1	6.8
5	3	7.9	8.3
0	4	13.2	13.0
1	4	35.1	31.3
2	4	18.6	16.1
3	4	6.0	5.2
4	4	5.7	5.4
5	4	6.3	6.6
0	5	29.2	28.7
1	5	2.9	2.4
2	5	9.3	7.8
3	5	11.3	10.3
4	5	8.3	9.6
5	5	1.9	1.2*
0	6	11.1	11.3
1	6	25.6	23.2
2	6	12.1	12.6
3	6	9.7	9.3
4	6	5.9	6.6
5	6	1.9	2.3*
0	7	15.6	14.4
1	7	7.7	7.1
2	7	8.4	8.1
3	7	16.5	17.0
4	7	6.9	7.5
0	8	13.3	13.9
1	8	6.4	6.8
2	8	9.3	9.5
3	8	4.9	4.7
4	8	6.6	6.9
0	9	1.9	1.7*
1	9	8.5	8.3
2	9	9.9	9.8
3	9	8.9	8.7
0	10	3.8	3.7
1	10	15.9	15.4
2	10	8.1	8.1
3	10	7.3	7.9
0	11	1.8	0.7*
1	11	4.3	4.4
******H= 2********			
0	0	22.5	23.0
1	0	15.4	14.5
2	0	9.3	7.7
3	0	12.0	9.4
4	0	1.9	1.7*
5	0	2.0	2.2*
6	0	1.9	1.0*
0	1	6.5	5.4
1	1	39.8	39.8
2	1	15.6	15.3
3	1	9.8	8.6
4	1	8.5	7.9
5	1	9.0	9.6
6	1	2.1	3.7*
0	2	82.9	84.1
1	2	27.7	27.6
2	2	8.4	9.1
4	2	5.8	5.3
5	2	8.6	9.0
6	2	4.7	5.4
0	3	1.4	0.6*
1	3	14.6	14.8
2	3	16.4	14.4
3	3	15.1	15.0
4	3	12.9	13.8
5	3	2.1	4.1*
0	4	38.5	36.7
1	4	36.7	34.3
2	4	14.3	13.0
4	4	3.4	1.8
5	4	9.1	8.8
0	5	34.4	34.1
1	5	4.3	4.3
2	5	19.9	19.2
3	5	17.4	17.8
4	5	6.3	7.2
5	5	3.1	2.3
0	6	22.5	23.6
1	6	21.1	20.0
2	6	5.0	5.0
3	6	4.4	5.5
4	6	5.5	5.7
5	6	2.8	1.9
0	7	10.0	10.5
1	7	12.4	12.1
2	7	6.8	7.4
3	7	1.9	1.3*
4	7	13.2	13.0
0	8	5.8	5.7
1	8	5.9	5.4
2	8	11.9	12.1
3	8	13.1	12.3
4	8	4.7	4.9
0	9	8.4	7.9
1	9	1.9	0.9*
3	9	7.5	6.8
0	10	11.8	12.0
1	10	11.3	11.9
2	10	15.1	14.6
3	10	1.9	1.4*
0	11	1.8	0.5*
1	11	7.9	7.1
******H= 3********			
1	0	96.3	98.7
2	0	7.2	6.7
3	0	1.6	2.0*
4	0	4.5	4.1
5	0	4.9	6.1
6	0	1.9	3.8*
0	1	32.3	32.0
1	1	35.7	38.5
2	1	19.3	19.8
3	1	24.9	22.6
4	1	11.4	11.7
5	1	5.0	4.5
6	1	4.8	4.7
0	2	83.1	81.3
1	2	22.1	22.6
2	2	16.0	16.4
3	2	6.5	7.8
4	2	8.6	9.4
5	2	4.1	5.7
0	3	11.3	10.0
1	3	24.6	24.1
2	3	6.0	5.4
3	3	17.4	16.8
4	3	7.7	8.8
5	3	9.3	10.8
0	4	36.8	35.7
1	4	10.1	9.0
2	4	25.4	25.1
3	4	4.2	5.1
4	4	8.5	8.3
5	4	8.9	7.8
0	5	2.5	2.3
1	5	17.9	17.6
2	5	16.6	15.9
3	5	5.4	6.2
4	5	6.2	6.7
5	5	2.0	2.4*
0	6	4.5	5.5
1	6	30.4	28.1
3	6	3.9	4.7
4	6	4.5	5.0
5	6	2.0	2.6*
0	7	5.2	5.8
1	7	8.4	7.7
2	7	3.9	3.7
3	7	5.0	6.0
4	7	8.4	9.2
0	8	1.8	1.0*
1	8	16.3	15.2
2	8	7.8	7.6
3	8	4.2	3.7
4	8	5.7	4.3
0	9	1.9	0.2*
1	9	11.3	11.6
2	9	8.8	8.5
3	9	8.9	8.1
0	10	6.0	5.9
1	10	3.5	3.4
2	10	4.8	4.7
0	11	7.4	7.8
1	11	2.9	3.2
******H= 4********			
0	0	106.4	109.9
1	0	14.9	14.9
2	0	24.7	22.6
3	0	9.8	10.8
4	0	4.7	3.8
5	0	3.4	4.1
0	1	9.7	11.5
1	1	38.1	38.6
2	1	7.9	6.4
3	1	11.8	12.6
4	1	6.6	6.1
5	1	4.0	4.5
0	2	17.7	16.6
1	2	31.2	31.4
2	2	21.4	20.4
3	2	1.7	3.4*
4	2	5.2	4.9
5	2	5.8	6.0
0	3	20.5	21.7
1	3	18.6	18.9
2	3	18.1	17.3
3	3	16.1	15.9
4	3	3.9	3.4
5	3	4.7	3.8
0	4	26.0	24.4
1	4	19.3	17.3
2	4	14.9	14.4
3	4	18.5	17.0
4	4	7.3	6.0
5	4	2.0	1.7*
0	5	11.3	11.9
1	5	25.2	22.9
2	5	7.6	6.5
3	5	5.5	4.9
5	5	7.9	7.7
1	6	12.9	12.5
2	6	9.6	7.7
3	6	5.4	4.6
4	6	10.1	10.7
5	6	3.7	3.3
0	7	12.7	12.3
1	7	5.6	6.1
2	7	6.4	7.2
3	7	13.1	14.4
0	8	1.8	1.2*
1	8	3.9	3.9
2	8	9.5	9.1
3	8	5.4	5.6
4	8	7.3	7.5
0	9	12.1	11.9
1	9	12.6	12.5
2	9	10.1	10.9
3	9	8.7	8.9
0	10	13.2	12.7
1	10	4.9	5.3
2	10	5.8	4.7
0	11	1.8	0.7*
1	11	5.9	6.0
******H= 5********			
1	0	50.2	49.7
2	0	6.3	8.6
3	0	1.8	2.0*
4	0	16.4	15.7
5	0	3.4	3.7
0	1	19.4	19.9
1	1	24.5	23.5
2	1	18.1	18.6
3	1	5.5	5.9
4	1	17.2	17.7
5	1	5.7	6.1
0	2	35.4	33.6
1	2	22.5	21.8
2	2	14.7	14.2
3	2	9.8	9.7
4	2	4.1	4.5
5	2	9.1	9.7
0	3	26.1	26.3
1	3	11.1	10.3
2	3	13.0	12.0
3	3	8.8	8.7
4	3	8.0	7.7
5	3	2.0	1.4*
0	4	15.8	14.1
1	4	23.6	21.3
2	4	7.1	8.3
3	4	8.3	7.3
4	4	6.1	5.0
5	4	1.9	1.1*
0	5	28.6	28.5
1	5	8.6	9.4
2	5	4.2	4.2
3	5	6.0	5.1
4	5	10.5	11.3
5	5	3.7	3.8
0	6	9.0	9.0
1	6	17.0	15.8
2	6	10.4	9.4
3	6	6.2	7.0
4	6	10.1	9.8
0	7	5.9	4.3
1	7	10.7	10.7
2	7	6.9	6.5
3	7	8.5	9.6
4	7	5.5	5.8
0	8	12.1	13.2
1	8	9.9	10.9
2	8	1.9	8.4*
3	8	4.5	5.7
0	9	5.3	6.3
1	9	7.1	6.8
2	9	8.9	8.2
0	10	6.7	6.4
1	10	8.0	7.2
2	10	3.5	1.8
0	11	3.1	3.7
******H= 6********			
0	0	22.6	24.8
1	0	10.6	10.5
2	0	3.1	1.9
3	0	14.4	13.9
4	0	9.4	8.1
5	0	7.9	7.1
0	1	10.1	8.4
1	1	15.9	13.1
2	1	26.0	28.0
3	1	16.5	18.1
5	1	11.6	10.7
0	2	26.4	26.4
1	2	35.8	34.6
2	2	14.4	14.0
3	2	1.8	2.4*
4	2	3.8	5.3
5	2	2.1	2.7*
0	3	3.7	2.8
1	3	1.5	1.4*
2	3	33.7	31.8
3	3	5.5	6.3
4	3	10.1	9.8
5	3	3.4	3.0
0	4	7.6	6.0
1	4	24.1	23.4
2	4	12.5	11.8
3	4	10.6	10.6
4	4	7.3	7.0
5	4	6.7	5.9
0	5	3.6	3.4
1	5	8.2	7.9
2	5	10.5	10.8
4	5	4.4	4.7
5	5	6.1	6.1
0	6	6.2	5.5
1	6	3.0	1.8
2	6	9.1	8.5
3	6	5.8	6.6
4	6	5.2	6.3
0	7	14.3	16.1
1	7	19.7	19.3
2	7	10.3	9.9
3	7	7.9	8.0
4	7	1.8	1.6*
0	8	9.9	10.2
1	8	14.4	15.5
2	8	8.4	8.4
3	8	5.1	4.1
0	9	9.9	10.6
1	9	6.1	5.5
2	9	6.7	6.3
3	9	6.4	6.0
0	10	3.7	4.5
1	10	5.6	4.9
******H= 7********			
1	0	2.4	2.7
2	0	3.4	3.8
3	0	6.3	6.3
4	0	7.5	6.0
5	0	10.1	9.1
0	1	9.4	8.0
1	1	22.3	20.3
2	1	9.4	9.6
3	1	1.8	2.4*
4	1	7.7	8.2
5	1	4.1	2.8
0	2	13.2	13.3
1	2	11.7	11.2
2	2	13.9	14.2
3	2	5.9	6.8
4	2	9.0	7.2
5	2	5.3	5.2
0	3	18.8	20.9
1	3	15.8	17.7
2	3	14.1	13.6
3	3	3.3	2.4
4	3	9.3	9.5
5	3	2.0	1.5*
0	4	1.6	2.2*
1	4	10.9	9.5
2	4	8.2	8.1
3	4	11.8	10.7
4	4	7.1	7.0
5	4	1.9	2.9*
0	5	5.5	5.9
1	5	5.5	5.2
2	5	5.9	3.4
3	5	3.4	3.6
4	5	7.1	8.0
0	6	1.8	3.3*
1	6	6.4	7.0
2	6	1.9	1.6*
3	6	6.7	7.1
4	6	4.0	4.1
0	7	10.2	12.6
1	7	3.5	4.3
2	7	9.2	9.5
3	7	1.9	0.1
4	7	6.1	6.7
0	8	3.6	2.7
1	8	4.6	5.7
2	8	5.9	5.7
3	8	2.9	2.6
0	9	6.9	7.7
1	9	10.0	11.3
2	9	8.9	9.7
0	10	1.8	2.2*
1	10	1.9	2.2*
******H= 8********			
0	0	8.7	8.0
1	0	4.2	3.6
2	0	17.6	15.1
3	0	5.7	5.0
4	0	3.6	5.0
5	0	13.6	12.6
0	1	22.3	20.9
1	1	18.3	18.2
2	1	18.7	17.4
3	1	12.1	12.3
4	1	7.9	7.8
5	1	4.7	3.3
0	2	1.6	2.4*
1	2	22.2	22.1
2	2	17.3	18.5
3	2	1.9	1.1*
4	2	9.3	8.2
5	2	2.9	2.5
0	3	15.2	15.5
1	3	30.8	30.8
2	3	17.7	17.7
3	3	8.0	7.
4	3	2.0	2.8*
5	3	1.9	2.4*
0	4	1.7	0.6*
1	4	22.1	23.2
2	4	14.1	14.5
3	4	4.6	5.0
4	4	8.0	8.2
0	5	4.5	5.5
1	5	9.8	8.8
2	5	3.5	3.6
3	5	3.4	2.6
4	5	3.6	3.8
0	6	1.8	2.2*
1	6	9.5	9.9
2	6	8.4	8.8
3	6	8.3	8.5
4	6	7.1	6.4
0	7	11.1	11.2
1	7	1.9	2.3*
2	7	8.4	7.9
3	7	10.2	11.0
0	8	12.5	13.4
1	8	6.6	5.6
2	8	9.2	9.5
3	8	1.9	1.0*
0	9	1.9	2.4*
1	9	10.0	9.9
2	9	5.1	4.9
0	10	1.8	0.3*
******H= 9********			
1	0	11.5	11.6
2	0	6.4	5.2
3	0	2.0	2.8*
4	0	12.2	12.0
5	0	2.1	5.4*
1	1	5.4	5.4
2	1	12.4	12.3
3	1	11.7	13.0
4	1	16.3	14.8
5	1	3.8	2.8
0	2	1.7	3.2*
1	2	9.5	9.4
2	2	12.7	13.5
3	2	5.8	7.0
4	2	1.9	1.0*
0	3	13.7	14.3
1	3	6.8	6.9
2	3	3.2	3.7
3	3	5.6	5.1
4	3	2.9	2.0
0	4	6.7	8.8
1	4	19.1	19.9
2	4	5.7	5.0
3	4	11.4	12.4
4	4	1.9	2.3*
0	5	9.5	8.9
1	5	7.6	8.6
2	5	4.0	4.3
3	5	3.1	3.7
4	5	6.4	6.0
0	6	1.9	2.4*
1	6	4.0	4.8
2	6	1.9	1.9*
3	6	4.2	3.7
0	7	12.8	13.8
1	7	14.1	14.4
2	7	9.7	9.7
3	7	4.4	4.4
0	8	9.3	9.6
1	8	7.8	7.4
2	8	6.0	5.7
0	9	2.8	2.7
1	9	10.6	11.6
******H=10********			
0	0	3.0	0.7
1	0	1.8	4.1*
2	0	7.8	7.0
3	0	11.9	11.3
4	0	5.3	4.8
0	1	12.9	11.7
1	1	6.2	5.7
2	1	7.3	7.5
3	1	5.2	4.7
4	1	3.9	1.7
0	2	6.5	6.3
1	2	18.9	17.9
2	2	6.6	6.4
3	2	3.7	3.7
4	2	5.3	5.1
0	3	15.8	16.1
1	3	6.2	6.5
2	3	6.9	5.3
3	3	5.9	5.2
4	3	2.0	3.6*
0	4	6.2	5.8
1	4	4.3	4.7
2	4	10.7	10.4
3	4	5.1	4.9
4	4	3.8	4.6
0	5	1.9	0.2*
1	5	10.4	10.2
2	5	12.0	12.4
3	5	4.1	3.4
4	5	1.9	1.5*
0	6	17.9	16.9
1	6	3.7	3.9
2	6	8.3	9.5
3	6	5.0	6.3
0	7	17.6	17.9
1	7	9.3	10.0
2	7	6.0	5.8
0	8	1.8	1.1*
1	8	5.1	6.1
2	8	4.3	4.4
0	9	10.2	11.4
******H=11********			
1	0	3.1	3.1
2	0	5.0	5.4
3	0	11.1	10.4
4	0	9.9	10.0
0	1	10.4	9.5
1	1	15.6	15.3
2	1	4.2	4.1
3	1	9.5	9.2
4	1	6.5	7.1
0	2	3.0	1.3
1	2	15.2	13.7
2	2	4.6	4.6
3	2	9.4	10.4
4	2	4.7	4.1
0	3	18.9	18.3
1	3	7.3	7.2
2	3	13.4	14.8
2	5	11.0	11.4
3	5	5.4	6.3
0	6	1.8	3.5
1	6	12.7	13.9
2	6	4.0	4.3
3	6	5.7	6.1
0	7	6.0	4.2
1	7	4.2	3.7
2	7	4.6	4.6
0	8	10.0	8.7
1	8	5.2	5.6
******H=12********			
0	0	5.0	5.3
1	0	1.9	0.7*
2	0	1.9	2.3*
4	0	7.9	8.5
0	1	1.9	0.4*
1	1	1.9	2.2*
-2	-1	3.2	2.5
******H=12********			
3	1	9.3	9.5
4	1	4.5	5.1
0	2	7.2	6.3
1	2	4.6	3.6
3	2	5.1	6.1
0	3	7.5	7.1
1	3	7.5	7.7
2	3	15.6	14.6
3	3	3.1	1.6
0	4	17.5	15.9
1	4	9.2	9.1
2	4	10.6	12.3
3	4	5.9	5.4
0	5	5.2	6.1
1	5	16.4	16.0
2	5	3.6	3.1
3	5	1.8	2.5*
0	6	3.7	4.5
1	6	3.9	4.5
2	6	4.0	3.9
0	7	1.8	0.3*
1	7	5.3	6.2
******H=13********			
1	0	4.8	6.1
2	0	7.5	7.0
3	0	2.8	1.2
0	1	4.2	3.6
1	1	3.3	4.1
2	1	1.9	1.0*
3	1	3.2	3.7
0	2	1.9	2.4*
1	2	7.7	7.8
2	2	7.9	8.5
3	2	4.2	4.4
0	3	2.0	1.2*
1	3	8.5	7.7
2	3	4.0	3.7
3	3	4.1	4.4
0	4	3.6	3.7
1	4	10.7	8.3
2	4	1.9	1.6*
0	5	18.8	17.5
1	5	5.3	5.0
0	6	1.8	2.0*
1	6	3.8	3.6
******H=14********			
0	0	2.0	1.5*
1	0	9.9	7.9
2	0	8.0	8.5
3	0	9.7	11.0
0	1	15.2	16.2
1	1	5.3	5.9
2	1	6.0	8.0
0	2	13.4	11.9
1	2	6.3	5.7
2	2	4.5	5.6
0	3	3.9	3.3
1	3	1.9	1.7*
2	3	1.9	1.2*
0	4	2.0	0.4*
1	4	6.2	6.7
2	4	1.8	1.0*
0	5	12.1	9.3
1	5	4.6	4.4
******H=15********			
1	0	1.9	3.2*
2	0	1.7	0.8*
0	1	6.9	7.2
1	1	4.0	3.9
2	1	3.0	3.2
0	2	1.9	0.8*
1	2	5.3	5.2
0	3	2.0	3.1*
1	3	1.9	2.1*
0	4	1.9	1.7*
******H=16********			
0	0	10.1	9.4

benzyl carbanion, and two half triethylenediamine cages. Both amines are related by the 2_1 screw operation in the *c* direction resulting in an empirical formula of one lithium atom per amine. Figure 3 shows the basic unit projected down the *b* axis along with a numbering scheme for future reference.

A least-squares best plane fit to the carbon atoms of the benzyl carbanion (Table VII) indicates that C(15) is pulled approximately 0.1 Å out of the plane of the phenyl ring toward the lithium atom. The average carbon–carbon distance in the benzyl ring is 1.40 (1) Å, and the average internal angle is 119.9 (8)°. The carb-

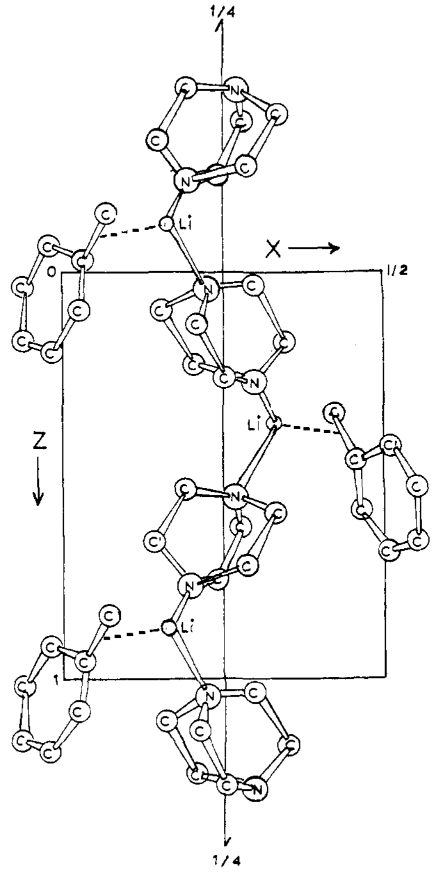

Figure 2. Polymeric nature of benzyllithium triethylenediamine.

anion nature of the ring is confirmed by two observations: (1) two terminal protons on C(15) were located by difference Fourier techniques; and (2) the C(15)–C(1) distance, 1.391 (1) Å, is typical for a carbon–carbon distance in a benzene type molecule.[33]

Table VI. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	R_1	R_2	R_3
C(15)	0.180	0.215	0.282
C(1)	0.178	0.209	0.260
C(2)	0.215	0.229	0.287
C(3)	0.218	0.267	0.292
C(4)	0.223	0.251	0.309
C(5)	0.194	0.216	0.331
C(6)	0.182	0.214	0.282
N(7)	0.166	0.196	0.251
C(8)	0.177	0.210	0.563
C(9)	0.161	0.188	0.647
N(10)	0.171	0.200	0.239
C(11)	0.176	0.224	0.611
C(12)	0.174	0.273	0.486
C(13)	0.167	0.232	0.444
C(14)	0.185	0.199	0.551
Li	0.122	0.178	0.233

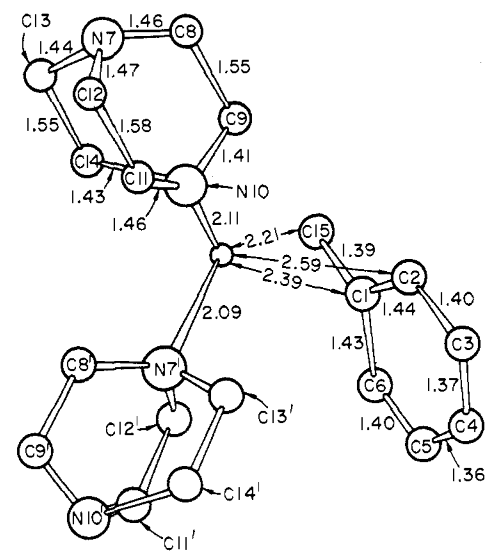

Figure 3. Molecular configuration of $C_6H_5CH_2^-Li^+N(C_2H_4)_3N$ viewed down the *b* axis. Hydrogen atoms are omitted for clarity.

The coordination of the lithium atom to the benzyl group is remarkably similar to that found for the molybdenum atom in *p*-methyl-π-benzyl-π-cyclopentadienyldicarbonylmolybdenum[34] (Figure 4). The lithium atom is located 2.21 (2) Å from C(15), 2.39 (2) Å from C(1), 2.58 (2) Å from C(2), and 3.38 (2) Å from C(6). Choosing C(15), N(10), and N(7) as an approximation to the lithium atom's coordination sphere, the cation is seen to be sp² hybridized with a depression of 0.20 (1) Å below this plane of coordination (Table V). Bond distances and angles given in Table VIII give an average Li–N distance of 2.10 (1) Å and average trigonal angle of 120.1 (7)°. The Li–N distance is slightly longer than previous reports of 2.01, 1.94, and 2.06 Å for $LiX \cdot 2NH_2CH_2CH_2NH_2$ (X = Cl, Br),[35a] $Li(NH_3)_4$,[35b] and LiCN,[36] respectively. This is the first known example of an sp² hybridized lithium atom in the solid state; its usual coordination number is four,

Table VII. Best Weighted Least-Squares Planes

Atoms	Plane	*A*	*B*	*C*	D^a
C(1)–C(6)	1	0.861	−0.395	−0.320	−3.026
C(15), C(1)–C(6)	2	0.849	−0.408	−0.335	−2.761
N(10), N(7)′, C(15)	3	−0.749	−0.655	−0.122	+7.900
N(10), N(7)′, C(15), Li	4	−0.744	−0.657	−0.121	+7.914

Atom	Distances from Planes, Å 1	2^b	3	4
C(15)	−0.103 (7)	−0.033 (7)	0.000	0.019 (8)
C(1)	0.006 (8)	0.043 (8)		
C(2)	−0.003 (9)	0.017 (8)		
C(3)	−0.001 (9)	−0.013 (10)		
C(4)	0.001 (9)	−0.028 (9)		
C(5)	0.009 (10)	−0.007 (10)		
C(6)	−0.007 (8)	0.010 (8)		
C(15)HA	0.004	0.086		
C(15)HB	−0.584	−0.501		
N(10)			0.000	0.012 (6)
N(7)′			0.000	0.019 (7)
Li	−2.004 (13)	−1.946 (13)	−0.198 (13)	−0.184 (13)

[a] The equation of the plane is given by $AX + BY + CZ + D = 0$. [b] This is the best plane through the carbanion.

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[33] E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc., Ser. A*, **247**, 1 (1958); for comparison the same distance in *p*-toluidine is 1.48. J. Wyart, *C. R. Acad. Sci., Paris*, **200**, 1862 (1935).

[34] F. A. Cotton and M. D. La Prade, *J. Am. Chem. Soc.*, **90**, 5418 (1968).

[35] (a) P. F. Durant, P. Durant, and M. Van Meerssche, *Acta Cryst.*, **23**, 780 (1967); (b) N. Mammano and M. J. Sienko, *J. Am. Chem. Soc.*, **90**, 23, 6322 (1968).

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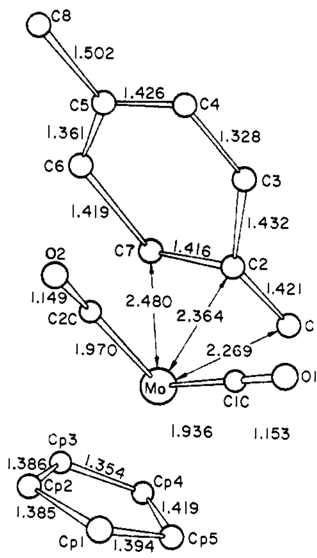

Figure 4. Molecular structure of *p*-methyl-π-benzyl-π-cyclopentadienyldicarbonylmolybdenum (ref 34).

as in the above-mentioned structures. In the crystallographic investigations of methyl-[3a] and ethyllithium,[3b] typical intramolecular carbon–lithium atom distances range from 2.19 to 2.28 Å and result from electron deficient bond formation.[4] Although distances C(15)–Li and C(1)–Li are in this range, the molecular geometry of the compound rules out any contributions of this type to the bonding.

Table VIII. Selected Intramolecular Distances and Angles

Atoms	Distance, Å	Atoms	Distance, Å
C(15)–C(1)	1.39 (1)	N(7)–C(8)	1.46 (1)
C(1)–C(2)	1.44 (1)	N(7)–C(12)	1.47 (1)
C(2)–C(3)	1.40 (1)	N(7)–C(13)	1.44 (1)
C(3)–C(4)	1.37 (1)	N(10)–C(9)	1.41 (1)
C(4)–C(5)	1.36 (1)	N(10)–C(11)	1.46 (1)
C(5)–C(6)	1.40 (1)	N(10)–C(14)	1.43 (1)
C(6)–C(1)	1.43 (1)	C(8)–C(9)	1.55 (1)
Li–C(15)	2.21 (2)	C(11)–C(12)	1.58 (2)
Li–C(1)	2.39 (2)	C(13)–C(14)	1.55 (2)
Li–N(10)	2.11 (1)	Li–C(15)HA	2.25
Li–N(7′)	2.09 (1)	Li–C(15)HB	2.54
Atoms	**Angle, deg**	**Atoms**	**Angle, deg**
C(15)–C(1)–C(2)	123.3 (8)	C(9)–N(10)–C(11)	105.7 (8)
C(15)–C(1)–C(6)	123.7 (7)	C(9)–N(10)–C(14)	109.8 (9)
C(2)–C(1)–C(6)	112.8 (5)	C(11)–N(10)–C(14)	106.3 (7)
C(1)–C(2)–C(3)	122.8 (9)	N(7)–C(8)–C(9)	109.8 (10)
C(2)–C(3)–C(4)	121.0 (8)	C(8)–C(9)–N(10)	112.6 (6)
C(3)–C(4)–C(5)	119.1 (6)	N(10)–C(11)–C(12)	111.6 (8)
C(4)–C(5)–C(6)	121.6 (9)	C(11)–C(12)–N(7)	109.2 (10)
C(8)–N(7)–C(12)	107.3 (7)	N(7)–C(13)–C(14)	110.4 (9)
C(8)–N(7)–C(13)	108.6 (7)	C(13)–C(14)–N(10)	112.3 (6)
C(12)–N(7)–C(13)	107.6 (6)	N(10)–Li–N(7′)	118.6 (4)
		C(15)–Li–N(10)	113.5 (5)
		C(15)–Li–N(7′)	125.3 (6)

One of our primary purposes in solving the crystal structure of this compound was to investigate the bonding forces in an intimate ion pair. Simple electrostatic arguments will place the lithium cation adjacent to the point of maximum electron density around the benzyl carbanion. Estimates of charge distributions in the carbanion have been obtained from Hückel molecular orbital calculations which indicate maximum total charge densities in the vicinity of C(15).[37] From an electrostatic viewpoint, the structural position of the lithium atom agrees well with this model. The lithium atom's approach distance to the carbanion is short enough, however, to imply that there is covalent character in the interaction as well. As a rough estimate of the amount of this interaction, the value of the radical probability density of a carbon $2p_z$ orbital was evaluated from C(15) out toward Li; both Clementi and Silverstone[38] orbitals were employed. For both types of orbitals the probabilities were greater than 20% at the lithium nucleus. Preliminary extended Hückel molecular orbital calculations in this laboratory indicate definite lithium 2s and 2p orbital contributions to the highest filled π molecular orbitals of the carbanion for the system $C_6H_5CH_2^-Li^+ \cdot 2NH_3$.[39] Covalent contributions to the bonding are therefore feasible. The dihedral angle between the planes of the carbanion and lithium atom coordination sphere is 84.6 (1.8)°. In terms of a covalent model, the lithium atom projects an sp^2 hybrid orbital into the π cloud. The strength of this interaction would be a function of the effective overlap between the two, and thus extremely sensitive to the lithium–benzyl distance.

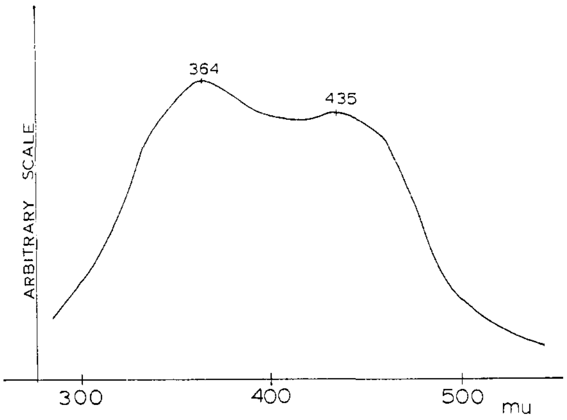

Figure 5. Mull spectrum of a crystalline sample of $C_6H_5CH_2^-Li^+N(C_2H_4)_3N$.

The measured solution spectrum of benzyllithium prepared in tetrahydrofuran exhibits a major transition at 330 mμ.[9] A previous orbital calculation by Bingle[40] on the benzyl carbanion predicts π–π* transitions at 328 and 413 mμ. In solution with sterically small donors, benzyllithium probably exists as a solvent separated ion pair with a tight solvation shell around the cation. The observed spectrum agrees with the theoretical one due to the presence of an essentially "free" carbanion. We have measured the solid mull spectrum of benzyllithium triethylenediamine (Figure 5) and find transitions at 364 and 435 mμ. Due to the perturbing influence of the amine-coordinated lithium cation, a pronounced bathochromic shift is noticeable relative to the theo-

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(39) We wish to thank Mr. Stan Anderson for the extended Hückel program and Mr. Ron Strange for valuable discussions on the topic.

(40) W. Bingle, *Z. Naturforsch.*, 10a, 476 (1955).

retical and solution spectra of the free carbanion. In solution, similar systems have exhibited bathochromic shifts when the cation size was increased.[41-43] For benzyllithium in tetrahydrofuran, a transition occurs at 330 mμ, while for benzylsodium, it occurs at 355 mμ. In these solutions, increasing the metal cation size decreases its ability to be solvated and therefore promotes association and increased perturbations of the π system of the carbanion. When a strongly coordinating but sterically bulky donor is present, such as triethylenediamine, 1,2-dimethoxyethane, or N,N,N′,N′-tetramethylethylenediamine, complete solvation of such small cations as Li^+ is not possible, and partially solvated species form. The carbanion can effectively compete with the donors in this situation and use its π cloud for complexation with the metal. Here the trend will be exactly opposite to the case of nonhindering solvents, with lithium exhibiting the largest bathochromic shift. The spectral results which have obtained here for benzyllithium triethylenediamine are consistent with this conclusion.

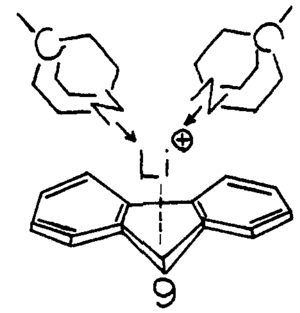

Figure 6. Predicted structure of fluorenyllithium–2-quinuclidine.

We are now in a position to predict in detail the geometry of other aromatic lithium systems. In fluorenyllithium, our molecular orbital calculations indicate that the lithium ion will penetrate the π cloud adjacent to the 9 position of the fluorenyl carbanion. Dixon has studied the structure of fluorenyllithium in solution using nuclear magnetic resonance techniques and has predicted a similar molecular arrangement.[11] The crystal structure and molecular properties of fluorenyllithium–2-quinuclidine are presently being determined in this laboratory (Figure 6), and will be reported in a subsequent publication.

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(42) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).
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The Chemistry of the Bis[π-(3)-1,2-dicarbollyl] Metalates of Nickel and Palladium

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Abstract: The synthesis, reactions, and structures associated with the "sandwich"-bonded bis[π-(3)-1,2-dicarbollyl] complexes of nickel and palladium, $[M^{n+}(1,2\text{-}B_9C_2H_{11})_2]^{n-4}$ (M = Ni, Pd), and their carbon-substituted derivatives are discussed. The nickel and palladium bis(dicarbollyl) systems each contain species with the metal atoms in the formal 2+ (d^8, two unpaired electrons for nickel, diamagnetic for palladium), 3+ (d^7, one unpaired electron), and 4+ (d^6, diamagnetic) oxidation states. X-Ray diffraction studies coupled with magnetic, spectral, and electrochemical data show that the d^8 M^{II} metal complexes suffer a slip-distortion from a symmetrical π sandwich; the d^7 M^{III} anions possess a symmetrical "nonslipped" sandwich structure, while the electrically neutral d^6 M^{IV} species maintain a "cisoid" sandwich configuration in which the carbon atom pairs on opposing ligands reside on the same side of the molecule. The uncharged $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2M^{IV}$ derivatives are Lewis acids, which form addition compounds with a variety of "soft" Lewis bases, *e.g.*, halide ions, thiocyanate ion, naphthalene, phenanthrene, pyrene, etc. The binding in these adducts appears to be primarily a dipole–induced dipole interaction arising from the high dipole moment of the nickel(IV) complex (6.16 D). The C,C′-dimethyl-substituted nickel and palladium systems, $M[1,2\text{-}B_9H_9C_2(CH_3)_2]_2$, exhibit facile thermal ligand rearrangement reactions leading to three isomeric series of complexes. In these isomerization reactions, a ligand carbon atom in the icosahedral surface was found to migrate away from the metal atom while remaining adjacent to the carbon atom in the open pentagonal face of the ligand. Similar rearrangements occur in the unsubstituted $Ni(1,2\text{-}B_9C_2H_{11})_2$ complex at 360–400° in the vapor phase. Cyclic voltammetry, optical resolution studies, and nmr data and their roles in the structure elucidation of these complexes are presented.

The (3)-1,2-dicarbollide ion, $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]^{2-}$ (Figure 1), has been shown to bond to a number of transition metals.[2-4] One feature associated with many of the "sandwich-bonded" bis(1,2-dicarbollyl) derivatives, $[M^{n+}(1,2\text{-}B_9C_2H_{11})_2]^{n-4}$, is their ability to undergo facile

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(1) (a) U. S. Public Health Service Predoctoral Fellow, 1966–1969; (b) Department of Chemistry, University of California, Los Angeles, Calif. 90024.
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