π Groups in Ion Pair Bonding. Fluorenyllithium Bisquinuclidine[1]

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Abstract: The crystal and molecular structure of fluorenyllithium bisquinuclidine, $C_{13}H_9Li(NC_7H_{13})_2$, has been determined from three-dimensional diffractometer data. The lattice parameters ($T = 23°$, $\lambda = 1.54178$ Å) are $a = 12.376$ (6), $b = 10.640$ (8), $c = 19.682$ (8) Å; $\beta = 118.13$ (4)° for the monoclinic unit cell and space group $P2_1/c$. The observed density is 1.15 (3) g/cc, while that calculated from the above lattice parameters is 1.15 g/cc for four molecules per unit cell. The final weighted R factor, $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$, was 0.073 for 2307 independent reflections. The disolvated lithium atom is located so that a perpendicular line from the lithium atom to the ring plane intersects the plane outside the five-membered ring at a point 1.09 Å from the closest boundary of the fluorenyl anion. The molecular geometry is not consistent with a simple electrostatic interpretation of the bonding but can be rationalized in terms of a substantial covalent interaction involving (1) a metal–carbanion three-center bond which is formed by an empty lithium orbital which is primarily p in character and two carbon p_z orbitals of the highest occupied molecular orbitals of the carbanion and (2) the σ overlap of a lithium sp^2 orbital with the lower energy bonding molecular orbitals of the carbanion. This interpretation is consistent with structural results obtained for benzyllithium, triphenylmethyllithium, and naphthalene(lithium)$_2$, with INDO and CNDO calculations for free carbanions and metal-complexed carbanions, and with nmr results reported previously for fluorenyllithium.

Recent research related to the study of complexes formed between π-organic groups and group I and IIa metals has resolved most of the macroscopic and a few of the molecular properties of these compounds.[2] It is, for example, well established that both solvent-separated and contact ion pair species are formed with distinct spectroscopic properties. The same studies have also revealed the prerequisites such as solvent, temperature, and concentration necessary to produce either the contact or solvent-separated system. Very little is currently known, however, about the actual molecular properties of these reagents. This includes anion geometry, metal ion solvation, and the site and nature of the metal ion interaction with the delocalized system. The goal of the research described in this and subsequent papers is to obtain sufficient structural data to understand and hopefully to be able to predict the detailed stereochemistry of π-carbanion organometallic complexes. Efforts will then be made to relate this information in a meaningful way to the solution chemistry of these compounds.

In this paper, the results of a single-crystal X-ray structural study of the solvated fluorenyllithium compound, fluorenyllithium bisquinuclidine, $C_{13}H_9Li(NC_7H_{13})_2$, are discussed.

Experimental Section

Fluorenyllithium bisquinuclidine was prepared[3] in an argon atmosphere drybox by combining 2 mmol each of fluorene, n-butyllithium, and quinuclidine in a mixture of 15 ml of hexane and 15 ml of ether. The resulting solution gradually turned bright yellow. The solution was allowed to stand undisturbed for 1–2 days during which time well-formed bright-yellow single crystals of the compound grew. These crystals were suitable for single-crystal X-ray analysis without further purification. Since $C_{13}H_9Li(NC_7H_{13})_2$ is very sensitive to oxygen and water, the crystals were mounted and sealed in thin-walled glass capillaries in an argon atmosphere.

Preliminary precession photographs showed the crystals to be monoclinic with systematic absences on $0k0$ for $k = 2n + 1$ and on $h0l$ for $l = 2n + 1$, uniquely determining the space group $P2_1/c$. A suitable crystal was chosen for structural analysis and mounted so that the rotation axis was offset slightly from the b^* axis to minimize the effects of multiple reflection.

Twelve reflections were carefully centered on a Picker four-circle diffractometer. These reflections formed the basis for a least-squares refinement of the lattice parameters ($T = 23°$, $\lambda = 1.54178$ Å) which, upon transformation to the standard $P2_1/c$ unit cell, yielded $a = 12.376$ (6), $b = 10.640$ (8), $c = 19.682$ (8) Å; $\beta = 118.13$ (4)°. The measured density of 1.15 (3) g/cc, obtained by the flotation method using a mixture of hexane and bromobenzene, is in excellent agreement with the calculated density of 1.15 g/cc corresponding to four molecules per unit cell.

The θ–2θ scan technique described previously[4] was used to collect a full form of data to $2\theta_{max} = 100.0°$. The intensities of 2307 independent reflections were measured of which 1230 were observed ($I_{obsd} > 3\sigma_c(I)$ where $\sigma_c = [T_c + 0.25\,(t_c/t_b)^2(B_1 + B_2)]^{1/2}$; T_c is the total integrated counts, t_c/t_b is the ratio of the time spent counting the peak intensity to the time spent counting the background intensities, and B_1 and B_2 are background counts). Weights were based on a modified Hughes scheme[5] with $\sigma = 4F_{min}/F_{obsd}$ for $F_{obsd} \leq 4F_{min}$ and $\sigma = F_{obsd}/4F_{min}$ for $F_{obsd} > 4F_{min}$ with F_{min} determined from $3\sigma_c(I)$. Unobserved reflections were weighted by arbitrarily assigning them a value of $\sigma = 12.0$. All of the unique form of data was used in the refinement. The justification for the use of the above weights has been given previously.[6] The details of the procedure used to correct the raw data and the structural solution are basically the same as for $(C_6H_5)_3CLi \cdot TMEDA$[4] and will not be described here. Full anisotropic refinement of all nonhydrogen atoms using all the unique form of data produced a final weighted

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[1] The support of the National Science Foundation and of the Advanced Research Projects Agency under Grant HC 15-67CO221 is gratefully acknowledged.

[2] (a) T. Ellingsen and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969); (b) I. B. Goldberg and J. R. Bolton, *ibid.*, **74**, 1965 (1970); (c) N. Hirota, R. Carraway, and W. Schook, *J. Amer. Chem. Soc.*, **90**, 3611 (1968); (d) R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967); (e) G. W. Canters, E. deBoer, B. M. P. Hendricks, and H. Van Willigen, *Chem. Phys. Lett.*, **1**, 627 (1968); (g) W. G. Williams, R. J. Pritchett, and G. F. Fraenkel, *J. Chem. Phys.*, **52**, 5584 (1970).

[3] This synthesis follows the general procedure outlined by A. W. Langer, Jr., U. S. Patent 3,541,149 (Nov 17, 1970).

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[6] S. C. Abrahams and J. M. Reddy, *J. Chem. Phys.*, **43**, 2583 (1965); S. C. Abrahams, *Acta Crystallogr., Sect. A*, **25**, 165 (1969).

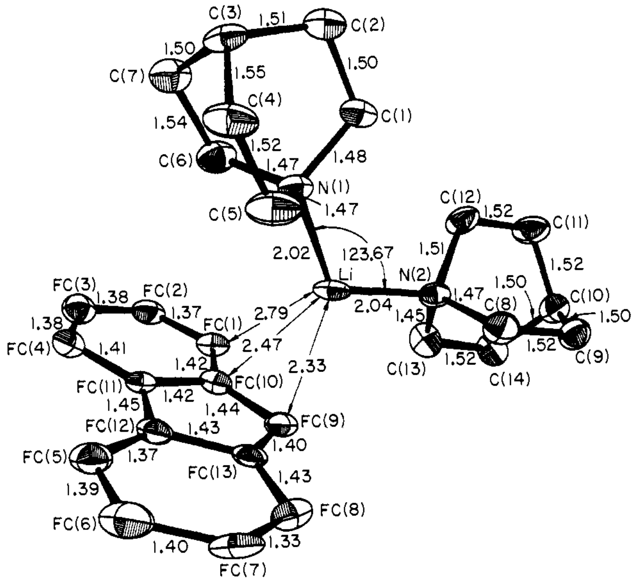

Figure 1. The molecular geometry of $C_{13}H_9Li(NC_7H_{13})_2$.

Table I. Positional Parameters for the Nonhydrogen Atoms in $C_{13}H_9Li(NC_7H_{13})_2$

Atom	x	y	z
Li	−0.0035 (9)[a]	−0.1198 (8)	0.1606 (6)
N(1)	−0.1141 (4)	−0.2362 (4)	0.0745 (2)
N(2)	0.1832 (4)	−0.1224 (4)	0.2095 (3)
C(1)	−0.0515 (6)	−0.3300 (6)	0.0493 (4)
C(2)	−0.1395 (6)	−0.4164 (5)	−0.0122 (3)
C(3)	−0.2700 (5)	−0.3812 (5)	−0.0335 (3)
C(4)	−0.2911 (6)	−0.2421 (6)	−0.0606 (3)
C(5)	−0.1988 (6)	−0.1637 (5)	0.0061 (4)
C(6)	−0.1889 (6)	−0.3072 (6)	0.1010 (3)
C(7)	−0.2856 (6)	−0.3902 (6)	0.0374 (4)
C(8)	0.2170 (6)	−0.0424 (5)	0.1618 (3)
C(9)	0.3550 (6)	−0.0356 (6)	0.1931 (4)
C(10)	0.4188 (5)	−0.1100 (6)	0.2663 (4)
C(11)	0.3769 (6)	−0.2456 (6)	0.2468 (4)
C(12)	0.2378 (6)	−0.2499 (5)	0.2116 (4)
C(13)	0.2426 (6)	−0.0770 (6)	0.2882 (4)
C(14)	0.3810 (6)	−0.0633 (6)	0.3237 (4)
FC(1)	−0.0841 (6)	−0.0876 (6)	0.2703 (3)
FC(2)	−0.1651 (8)	−0.1568 (5)	0.2842 (4)
FC(3)	−0.2902 (7)	−0.1479 (5)	0.2377 (4)
FC(4)	−0.3374 (5)	−0.0670 (6)	0.1756 (4)
FC(5)	−0.3884 (6)	0.1368 (6)	0.0372 (4)
FC(6)	−0.3835 (7)	0.2218 (7)	−0.0152 (4)
FC(7)	−0.2679 (8)	0.2604 (5)	−0.0039 (4)
FC(8)	−0.1627 (6)	0.2228 (6)	0.0550 (4)
FC(9)	−0.0710 (5)	0.0782 (5)	0.1750 (4)
FC(10)	−0.1286 (6)	−0.0031 (5)	0.2069 (3)
FC(11)	−0.2576 (6)	0.0058 (5)	0.1586 (3)
FC(12)	−0.2816 (6)	0.0945 (5)	0.0972 (3)
FC(13)	−0.1641 (6)	0.1344 (5)	0.1090 (3)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

R factor

$$R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2} = 0.073$$

The estimated standard deviation of an observation of unit weight (ERF) given by $[\Sigma w(F_o - F_c)^2[(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables, was 2.02. Tables I and II give the final positional and thermal parameters, while Tables III and IV give the interatomic distances and angles.[7]

Discussion

The structure of $C_{13}H_9Li(NC_7H_{13})_2$ found by this analysis is given in Figure 1. The location of the lithium atom with respect to the fluorenyl group differs somewhat from the metal positions suggested by Dixon in fluorenyllithium[8a] and Hogen-Esch and Smid in bisfluorenylbarium.[8b] Both of these previous studies are interpreted in terms of the metal atom being directly above the plane and within the periphery of the inner five-membered ring of the fluorenyl carbanion. It might also be noted that the metal atom in $C_5H_5MgBr[(C_2H_5)_2NCH_2CH_2N(C_2H_5)_2]$[9] is located above the center of the C_5H_5 ring. The metal atom in $C_{13}H_9Li(NC_7H_{13})_2$ is located above the ring plane; however, the position of the lithium atom is not within the periphery of the five-membered ring. A perpendicular line from the lithium atom to the ring plane intersects the plane outside the five-membered ring at a point (A) 1.09 Å from the closest point (B) on the boundary of the fluorenyl anion. B is located 0.48 Å from FC(9) on the FC(9)–FC(10) bond. The distances to point A from FC(9), FC(10), and FC(1) are 1.11, 1.30, and 1.90 Å, respectively.

The coordination sphere of the lithium atom is made up of two tertiary amines and one unsaturated organic group. This reaffirms the coordination number of 3 for lithium in amine-solvated unsaturated organolithium compounds that was first established in benzyllithium triethylenediamine.[10] The average Li–N distance in fluorenyllithium bisquinuclidine is 2.030 (9) Å, while in benzyllithium triethylenediamine it is 2.100 (8) Å. As discussed previously, the difference is the result of differences in the stabilities of the benzyl and fluorenyl carbanions and the greater base strength of quinaclidine compared to the dibasic triethylenediamine.

The fluorenyl carbanion deviates somewhat from planarity (plane 1, Table V). The two outer six-membered rings and the inner five-membered ring are planar within experimental error. The benzyl fragment that is more closely associated with the lithium carbanion (plane 5, Table V) shows a significant deviation from planarity while the other benzyl fragment (plane 6, Table V) is planar within experimental error. The nonplanarity of the benzyl fragment (plane 5, Table V) can best be described as a deviation of FC(9) from the plane of the six-membered ring (plane 2, Table V). Considering this plane, one sees that FC(9) is pulled 0.04 Å out of the plane toward the lithium atom. This can be compared with the 0.10-Å deviation toward the lithium atom of the benzylic carbon in benzyllithium triethylenediamine.[10] The 0.04-Å deviation of FC(9) is reasonable considering that the FC(9) position is much more restricted than the benzylic carbon in benzyllithium due to the fact that it is part of a five-membered ring. An examination of the molecular

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(7) A listing of structure factor amplitudes and of the calculated hydrogen atom positions will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7339. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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Table II. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in $C_{13}H_9Li(NC_7H_{13})_2$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Li	0.0161 (12)	0.0047 (9)	0.0060 (5)	0.0014 (9)	0.0045 (7)	−0.0009 (5)
N(1)	0.0140 (5)	0.0069 (5)	0.0038 (2)	−0.0008 (5)	0.0040 (3)	−0.0003 (3)
N(2)	0.0119 (5)	0.0075 (5)	0.0037 (2)	0.0008 (5)	0.0027 (3)	0.0009 (3)
C(1)	0.0144 (8)	0.0096 (7)	0.0074 (4)	−0.0002 (7)	0.0055 (5)	−0.0025 (4)
C(2)	0.0157 (8)	0.0077 (7)	0.0045 (3)	0.0004 (6)	0.0032 (4)	−0.0007 (4)
C(3)	0.0126 (7)	0.0055 (6)	0.0037 (3)	0.0003 (5)	0.0009 (3)	−0.0003 (3)
C(4)	0.0185 (9)	0.0091 (7)	0.0039 (3)	0.0027 (7)	0.0020 (4)	0.0000 (4)
C(5)	0.0218 (9)	0.0090 (7)	0.0044 (3)	0.0022 (7)	0.0029 (5)	0.0006 (4)
C(6)	0.0179 (8)	0.0129 (7)	0.0042 (3)	−0.0022 (7)	0.0047 (5)	−0.0010 (4)
C(7)	0.0179 (9)	0.0111 (7)	0.0051 (3)	−0.0016 (7)	0.0053 (5)	−0.0007 (4)
C(8)	0.0129 (8)	0.0107 (7)	0.0054 (3)	0.0028 (6)	0.0034 (4)	0.0021 (4)
C(9)	0.0134 (8)	0.0108 (8)	0.0076 (4)	0.0004 (6)	0.0049 (5)	0.0015 (4)
C(10)	0.0122 (7)	0.0118 (7)	0.0053 (3)	−0.0008 (6)	0.0035 (4)	−0.0001 (4)
C(11)	0.0136 (8)	0.0085 (8)	0.0088 (4)	0.0025 (7)	0.0037 (5)	0.0000 (4)
C(12)	0.0121 (8)	0.0071 (7)	0.0094 (4)	0.0007 (6)	0.0042 (5)	0.0013 (4)
C(13)	0.0131 (8)	0.0177 (9)	0.0046 (3)	0.0018 (7)	0.0030 (4)	0.0000 (4)
C(14)	0.0118 (9)	0.0190 (9)	0.0055 (3)	−0.0005 (7)	0.0027 (5)	−0.0029 (5)
FC(1)	0.0143 (8)	0.0071 (7)	0.0039 (3)	0.0009 (7)	0.0029 (4)	−0.0006 (4)
FC(2)	0.0175 (10)	0.0076 (7)	0.0057 (4)	0.0015 (7)	0.0061 (5)	0.0008 (4)
FC(3)	0.0149 (9)	0.0091 (7)	0.0055 (5)	0.0002 (7)	0.0055 (5)	0.0003 (4)
FC(4)	0.0111 (7)	0.0093 (7)	0.0055 (3)	0.0012 (7)	0.0037 (4)	−0.0013 (4)
FC(5)	0.0125 (8)	0.0078 (7)	0.0049 (3)	0.0000 (6)	0.0024 (5)	−0.0016 (4)
FC(6)	0.0145 (9)	0.0083 (8)	0.0052 (3)	0.0022 (7)	0.0012 (5)	−0.0006 (4)
FC(7)	0.0163 (10)	0.0043 (6)	0.0055 (3)	0.0000 (7)	0.0018 (5)	−0.0004 (4)
FC(8)	0.0145 (9)	0.0072 (7)	0.0048 (3)	−0.0024 (6)	0.0037 (5)	−0.0010 (4)
FC(9)	0.0100 (7)	0.0057 (6)	0.0052 (3)	0.0003 (6)	0.0030 (4)	−0.0008 (4)
FC(10)	0.0113 (8)	0.0068 (6)	0.0039 (3)	0.0015 (6)	0.0031 (4)	−0.0008 (4)
FC(11)	0.0101 (8)	0.0058 (6)	0.0045 (3)	0.0000 (6)	0.0033 (4)	−0.0015 (4)
FC(12)	0.0092 (7)	0.0067 (6)	0.0040 (3)	0.0016 (6)	0.0014 (4)	−0.0013 (4)
FC(13)	0.0100 (8)	0.0059 (6)	0.0045 (3)	0.0005 (6)	0.0023 (4)	−0.0021 (4)

[a] The form of the anisotropic thermal elipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Interatomic Distances (Å) for the Nonhydrogen Atoms[a] in $C_{13}H_9Li(NC_7H_{13})_2$

Atoms	Distance	Atoms	Distance
Li–N(1)	2.021 (11)	C(10)–C(11)	1.520 (8)
Li–N(2)	2.040 (11)	C(10)–C(14)	1.497 (8)
Li–FC(9)	2.333 (10)	C(11)–C(12)	1.522 (8)
Li–FC(10)	2.471 (11)	C(13)–C(14)	1.521 (8)
Li–FC(1)	2.794 (13)	FC(1)–FC(2)	1.371 (8)
N(1)–C(1)	1.485 (6)	FC(1)–FC(10)	1.421 (7)
N(1)–C(5)	1.474 (7)	FC(2)–FC(3)	1.380 (8)
N(1)–C(6)	1.468 (7)	FC(3)–FC(4)	1.379 (8)
C(1)–C(2)	1.499 (7)	FC(4)–FC(11)	1.413 (7)
C(2)–C(3)	1.512 (7)	FC(5)–FC(12)	1.367 (7)
C(3)–C(4)	1.553 (8)	FC(5)–FC(6)	1.394 (8)
C(3)–C(7)	1.499 (8)	FC(6)–FC(7)	1.402 (8)
C(4)–C(5)	1.518 (8)	FC(7)–FC(8)	1.331 (8)
C(6)–C(7)	1.538 (8)	FC(8)–FC(13)	1.425 (7)
N(2)–C(8)	1.468 (7)	FC(9)–FC(10)	1.439 (7)
N(2)–C(12)	1.508 (7)	FC(9)–FC(13)	1.400 (7)
N(2)–C(13)	1.448 (7)	FC(10)–FC(11)	1.424 (7)
C(8)–C(9)	1.518 (8)	FC(11)–FC(12)	1.449 (7)
C(9)–C(10)	1.501 (8)	FC(12)–FC(13)	1.426 (7)

[a] Errors in the lattice parameters are included in the estimated standard deviations.

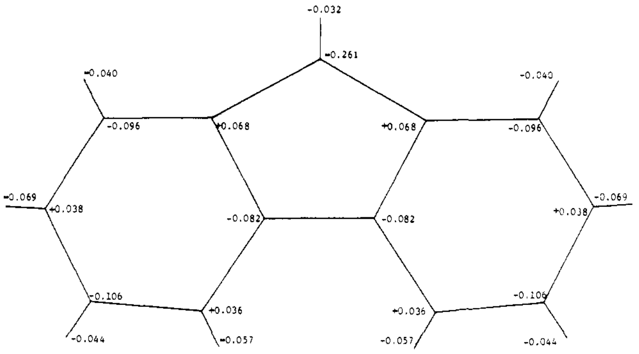

Figure 2. Gross atomic charges from the CNDO molecular orbital calculation for the fluorenyl carbanion.

packing in the unit cell reveals no unusual nonbonding contacts.

Primarily because of the reputation of group IA compounds to form predominantly ionic bonds, it is tempting to invoke an electrostatic interpretation of the lithium–fluorenyl interaction. Simple Hückel molecular orbital calculations[11,12] for the fluorenyl carbanion indicate that the greatest π-electron density is located at the FC(9) position. Thus, from a purely ionic argument, one would predict the observed fact that the closest approach of the lithium cation to any carbon atom in the fluorenyl ring (2.33 Å) is to FC(9). A somewhat more rigorous evaluation of the atomic charges obtained from a CNDO II molecular orbital calculation[13] including hydrogen atoms gives the distribution indicated in Figure 2. The electrostatic potential energy for this distribution of point charges is shown in Figure 3. From these results, it is to be expected that the lithium atom would be located over the potential energy minima, within the periphery of the five-membered ring. In fact, the observed position of the lithium atom is approximately 1.5 Å away from this location. An examination of the CNDO and INDO charge distribution for benzyllithium gives results (Figure 4) similar to those obtained for fluorenyllithium. The potential energy minimum is located

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Table IV. Bond Angles (deg) for the Nonhydrogen Atoms in $C_{13}H_9Li(NC_7H_{13})_2$

Atoms	Angle	Atoms	Angle
N(1)–Li–N(2)	123.7 (5)[a]	C(11)–C(10)–C(14)	108.4 (6)
Li–N(1)–C(1)	116.0 (5)	C(10)–C(11)–C(12)	108.7 (5)
Li–N(1)–C(5)	110.7 (5)	C(11)–C(12)–N(2)	112.5 (5)
Li–N(1)–C(6)	107.9 (5)	N(2)–C(13)–C(14)	114.6 (5)
C(1)–N(1)–C(5)	107.7 (5)	C(13)–C(14)–C(10)	107.9 (5)
C(1)–N(1)–C(6)	106.8 (4)	F(10)–FC(1)–FC(2)	119.9 (5)
C(5)–N(1)–C(6)	107.4 (5)	FC(1)–FC(2)–FC(3)	121.9 (6)
N(1)–C(1)–C(2)	112.8 (5)	FC(2)–FC(3)–FC(4)	120.2 (6)
C(1)–C(2)–C(3)	110.2 (5)	FC(3)–FC(4)–FC(11)	120.0 (6)
C(2)–C(3)–C(4)	108.4 (5)	FC(12)–FC(5)–FC(6)	119.4 (6)
C(2)–C(3)–C(7)	108.5 (5)	FC(5)–FC(6)–FC(7)	118.1 (6)
C(4)–C(3)–C(7)	107.8 (5)	FC(6)–FC(7)–FC(8)	123.8 (6)
C(3)–C(4)–C(5)	106.9 (5)	FC(7)–FC(8)–FC(13)	119.7 (6)
C(4)–C(5)–N(1)	114.9 (5)	FC(10)–FC(9)–FC(13)	107.6 (5)
N(1)–C(6)–C(7)	112.7 (5)	FC(9)–FC(10)–FC(1)	134.2 (6)
C(6)–C(7)–C(3)	109.1 (5)	FC(9)–FC(10)–FC(11)	107.4 (5)
Li-N(2)–C(8)	107.0 (4)	FC(1)–FC(10)–FC(11)	118.4 (6)
Li-N(2)–C(12)	114.7 (4)	FC(10)–FC(11)–FC(4)	119.6 (6)
Li–N(2)–C(13)	113.0 (5)	FC(10)–FC(11)–FC(12)	108.9 (5)
C(8)–N(2)–C(12)	106.2 (4)	FC(4)–FC(11)–FC(12)	131.5 (6)
C(8)–N(2)–C(13)	109.7 (5)	FC(11)–FC(12)–FC(13)	105.5 (6)
C(12)–N(2)–C(13)	106.1 (5)	FC(11)–FC(12)–FC(5)	132.0 (6)
N(2)–C(8)–C(9)	112.1 (5)	FC(5)–FC(12)–FC(13)	122.5 (6)
C(8)–C(9)–C(10)	110.1 (5)	FC(9)–FC(13)–FC(12)	110.6 (6)
C(9)–C(10)–C(11)	107.2 (5)	FC(8)–FC(13)–FC(9)	132.9 (6)
C(9)–C(10)–C(14)	109.8 (6)	FC(8)–FC(13)–FC(12)	116.5 (5)

[a] Errors in lattice parameters are included in the estimated standard deviations.

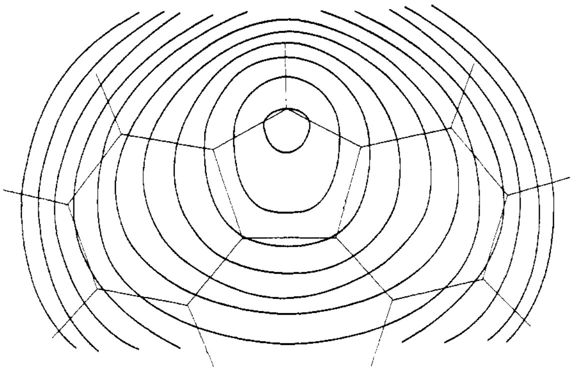
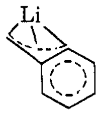


Figure 3. Potential energy surface at 2.0 Å above the plane of the fluorenyl carbanion calculated from the CNDO II atomic charge distribution. Contour lines are drawn at levels of 0.02 eV.

on the α-carbon-ring carbon bond approximately 0.4 Å from the α-carbon position (Figure 5). Finally, the lithium atom is also displaced from the position predicted by electrostatic calculations for the triphenylmethyl carbanion.[4]

The alternative description of the Li–C(1) bond as a two-center covalent σ bond analogous to the saturated carbon–hydrogen bond in cyclopentadiene, toluene, or fluorene would result in the lithium atom being located on the mirror plane normal to the ring plane of these hydrocarbons and coordinated to a carbon atom valence orbital directed away from the center of the organic molecule. The structural results obtained from studies of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$,[4] $C_6H_5CH_2Li \cdot N(CH_2)_3N$,[16] and $C_{13}H_9Li(NC_7H_{13})_2$ clearly show that this is not the case. All the organic groups have the features expected for completely delocalized π carbanions and the actual disposition of the lithium atom with respect to a benzylic fragment in these molecules is that shown below.



In these compounds, the lithium atom distance to the plane not containing the most negative atom or atoms is approximately 2.0 Å.

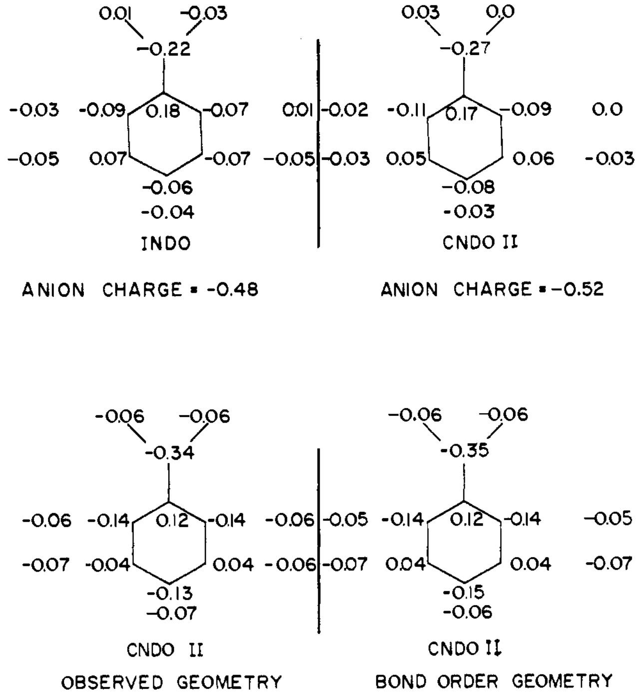


Figure 4. CNDO II and INDO charge distributions for the benzyl carbanion. The top two configurations are for the $Li(NH_3)_2$-complexed carbanions and the bottom for the isolated carbanion with a charge of −1.

Table V. Mean Least-Squares Planes for $C_{13}H_9Li(NC_7H_8)_2$

Plane	Atoms in plane	Equation of plane[a,b]
1	FC(1), FC (2), FC (3), FC (4), FC(5), FC(6), FC(7), FC(8), FC(9), FC(10), FC(11), FC(12), FC(13)	$0.3435x - 0.7466y - 0.5695z + 3.1989 = 0$
2	FC(1), FC(2), FC(3), FC(4), FC(10), FC(11)	$0.3551x - 0.7322y - 0.5811z + 3.3059 = 0$
3	FC(5), FC(6), FC(7), FC(8), FC(12), FC(13)	$0.3276x - 0.7592y - 0.5623z + 3.1515 = 0$
4	FC(9), FC(10), FC(11), FC(12), FC(13)	$0.3381x - 0.7541y - 0.5629z + 2.1813 = 0$
5	FC(1), FC(3), FC(3), FC(4), FC(9), FC(10), FC(11)	$0.3484x - 0.7375y - 0.5784z + 0.2583 = 0$
6	FC(5), F3(6), FC(7), FC(8), FC(9), FC(12), FC(13)	$0.3285x - 0.7599y - 0.5608z + 3.1555 = 0$

	Deviations of atoms from planes, Å					
Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
FC(1)	0.004 (6)	0.002 (6)			−0.004 (6)	
FC(2)	0.028 (7)	−0.001 (7)			0.005 (7)	
FC(3)	0.032 (7)	0.002 (7)			0.012 (7)	
FC(4)	0.001 (6)	−0.005 (6)			−0.002 (7)	
FC(5)	−0.025 (7)		−0.004 (7)			−0.005 (7)
FC(6)	0.004 (7)		−0.001 (7)			−0.003 (7)
FC(7)	0.042 (7)		0.011 (7)			0.010 (7)
FC(8)	0.019 (7)		−0.011 (7)			−0.010 (7)
FC(9)	−0.013 (6)	0.042 (6)	−0.009 (6)	−0.003 (6)	0.015 (6)	−0.003 (7)
FC(10)	−0.029 (6)	−0.005 (6)		−0.004 (6)	−0.019 (6)	
FC(11)	−0.016 (6)	0.006 (6)		0.009 (6)	−0.004 (6)	
FC(12)	−0.020 (6)		0.001 (6)	−0.011 (6)		0.003 (6)
FC(13)	0.008 (6)		0.005 (6)	0.009 (6)		0.008 (6)
Li	2.036 (10)	2.075 (10)	2.049 (10)	2.055 (10)	2.052 (10)	2.057 (10)

The dihedral angle between planes 2 and 3 is 2.5°
The dihedral angle between planes 5 and 6 is 2.0°
The dihedral angle between planes 2 and 4 is 1.9°
The dihedral angle between planes 3 and 4 is 0.7°

[a] The orthogonal unit cell vectors a', b', c' are related to the monoclinic vectors a, b, c as follows: $(a', b', c') = (a + c \cos \beta, b, c \sin \beta)$.
[b] The weight of each atom is inversely proportional to the mean variance of the positional parameters for that atom.

The above structural features suggest that a covalent three-center contribution to the bonding may be responsible for the observed configurations. In a simple valence bond picture, the lithium atom is pictured as being sp^2 hybridized with two sp^2 orbitals to bond with the two nitrogen atoms (the observed N–Li–N angle is ~120° for monodentate amine bases) and the remaining sp^2 orbital is coordinated to the aromatic ring. The unhybridized p orbital parallel to the ring plane can then form a bond with the π cloud of the fluorenyl carbanion. An additional structural requirement dictated by this model is that the N–Li–N group be oriented so that the lithium p orbital parallel to the ring plane can overlap favorably with the carbon p orbitals normal to the ring plane. In order to investigate this interaction, it is necessary to examine the symmetry of the molecular orbitals which contain substantial contributions from these atomic orbitals. The bond lengths in the carbanions in the structures which we have examined are close to those expected from simple Hückel bond orders. We conclude from this that the carbanion π-orbital contribution to the highest occupied molecular orbital (HOMO) of the complex is probably very similar to the HOMO of the free carbanion which is made up almost entirely of carbon atom p_z orbitals. The symmetries of the HOMO's of the free benzyl and fluorenyl carbanions and the orientation of the N–Li–N groups with respect to the carbanions are displayed in Figures 6 and 7. It can be seen that the N–Li–N group is positioned in such a way as to give

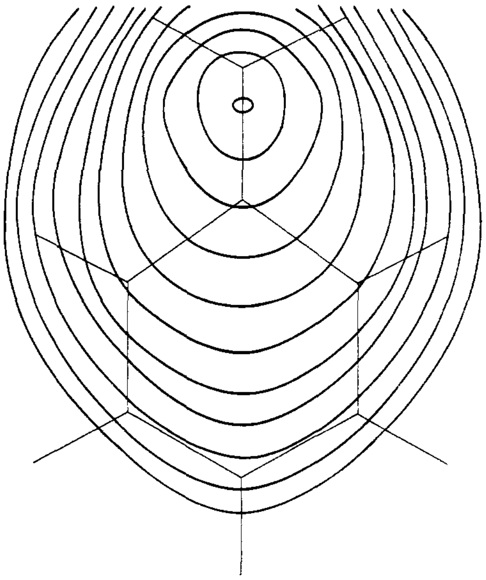
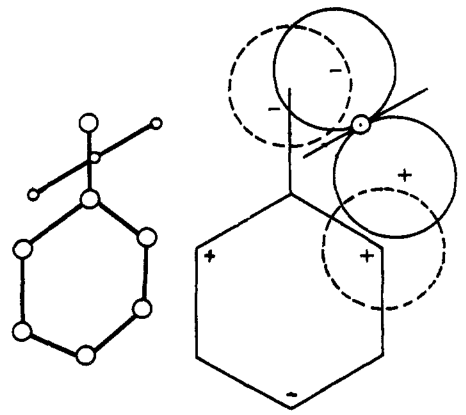


Figure 5. Potential energy surface at 2.0 Å above the plane of the phenyl ring of the isolated benzyl carbanion calculated from the CNDO II atomic charge distribution. Contour lines are drawn at levels of 0.02 eV.



Benzyl Lithium

Figure 6. Symmetry of the highest occupied molecular orbital (carbon p_z atomic orbitals) of the isolated benzyl carbanion and orientation of the LiN_2 group with respect to the carbanion plane. The figure to the left is the projection as viewed along the bisector of the N–Li–N angle, while that to the right is the projection onto the phenyl ring plane. The orientation of the LiN_2 group is indicated by the dark straight lines intersecting at the lithium atom position in the latter figure.

maximum overlap of the lithium p orbital which is parallel to the carbanion plane and the appropriate p_z orbitals of carbon atoms in the plane. The orientation of the N_2Li group in naphthalenide $(LiTMED)_2$[14] is also consistent with that predicted by symmetry considerations of the HOMO of the free carbanion.

In order to further investigate the nature of the metal–carbanion interaction, INDO and CNDO II calculations were carried out on model complexes. The results for benzyllithium will be discussed first. The INDO molecular orbital coefficients for the HOMO of the benzyl carbanion are given in Table VI. As indicated above, the symmetry of this orbital is appropriate for overlap between the C_2 and C_7 p_z orbitals and

Table VI. INDO Molecular Orbital Results for the Highest Occupied Molecular Orbitals in the Benzyl Carbanion and in the Complex $(NH_3)_2LiC_7H_7$

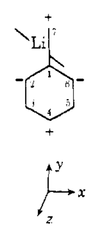
Benzyl Carbanion

$$\Psi = 0.04p_z{}^1 - 0.41p_z{}^2 + 0.00p_z{}^3 + 0.41p_z{}^4 + 0.00p_z{}^5 - 0.41p_z{}^6 + 0.69p_z{}^7$$

Benzyl $Li(NH_3)_2$

$$\Psi = -0.17p_x{}^{Li} - 0.24p_y{}^{Li} - 0.08s^{Li} - 0.07p_z{}^1 - 0.36p_z{}^2 + 0.10p_z{}^3 + 0.39p_z{}^4 + 0.00p_z{}^5 - 0.40p_z{}^6 + 0.65p_z{}^7$$

Overlap Integrals

C–Li	S_{ab}	C–Li	S_{ab}	
$p_z{}^1 - p_x$	0.11	$s^1 - p_z$	0.35	
$p_z{}^1 - p_y$	0.09	$s^2 - p_z$	0.29	
$p_z{}^2 - p_x$	0.02	$p_z{}^1 - s$	0.12	
$p_z{}^2 - p_y$	0.14	$p_z{}^2 - s$	0.11	
$p_z{}^7 - p_x$	0.13	$p_z{}^7 - s$	0.13	
$p_z{}^7 - p_y$	0.07	C–C		
$s^7 - p_z$	0.39	$p_z{}^1 - p_z{}^2$	0.23	
$s^7 - s$	0.32	$s^1 - s^2$	0.39	
$s^1 - s$	0.28	$s^2 - p_y{}^3$	0.41	
$s^2 - s$	0.25			

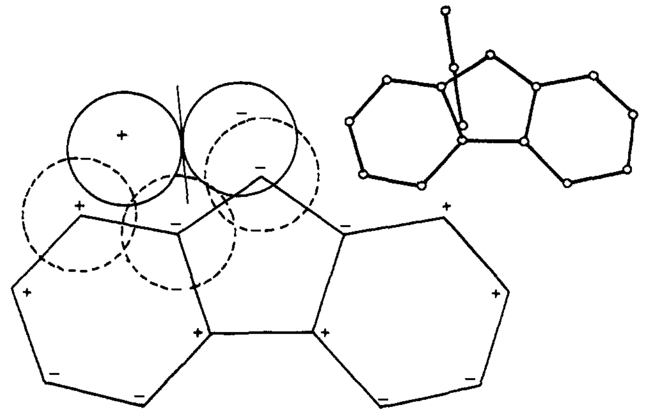


Figure 7. As in Figure 6, for fluorenyllithium, the projection as viewed along the bisector of the LiN_2 group is to the upper right. The lower left projection is along the normal to the mean plane of the fluorenyl carbanion.

a combination of lithium p_x and p_y orbitals. In addition, we note the relatively small contribution of the C_1 p_z orbital to the HOMO. The HOMO of the complex $Li(NH_3)_2 \cdot C_7H_7$ (Table VI) is made up of the HOMO of the carbanion and the Li p_x and p_y orbitals with a substantially smaller proportion of Li p_z. The values of the overlap integrals $Li(p_x,p_y)$–$C(p_z)$ and, for comparison, the value of the $C(p_z)$–$C(p_z)$ overlap integral for adjacent carbon atoms in the benzyl carbanion are also given. We conclude that both symmetry and INDO calculations are consistent with a substantial degree of three-center carbanion–metal bonding of the type described above. The corresponding results for the fluorenyl carbanion (Table VII) lead to the same conclusions. Because of the twisting of the phenyl rings in the triphenylmethyl carbanion and the interaction of the lithium atom with two phenyl rings instead of one, a similar localized valence bond picture for this carbanion is not as easily described; however, CNDO results for $(NH_3)_2LiHC(C_6H_5)_2$ also suggest that the Li

Table VII. CNDO Molecular Orbital Results for the Highest Occupied Molecular Orbital in the Fluorenyl Carbanion and in the Complex $Li(NH_3)_2C_{13}H_9$

Fluorenyl Anion

$$\Psi = -0.30p_z{}^1 - 0.09p_z{}^2 + 0.32p_z{}^3 + 0.13p_z{}^4 + 0.13p_z{}^5 + 0.32p_z{}^6 - 0.09p_z{}^7 - 0.30p_z{}^8 + 0.61p_z{}^9 + 0.06p_z{}^{10} - 0.31p_z{}^{11} - 0.31p_z{}^{12} + 0.06p_z{}^{13}$$

Fluorenyl $Li(NH_3)_2$

$$\Psi = 0.05s^{Li} + 0.17p_x{}^{Li} + 0.01p_y{}^{Li} - 0.07p_z{}^{Li} - 0.28p_z{}^1 - 0.06p_z{}^2 + 0.28p_z{}^3 + 0.13p_z{}^4 + 0.15p_z{}^5 + 0.37p_z{}^6 - 0.04p_z{}^7 - 0.33p_z{}^8 + 0.58p_z{}^9 + 0.05p_z{}^{10} - 0.26p_z{}^{11} - 0.32p_z{}^{12} - 0.06p_z{}^{13}$$

Overlap Integrals

C–Li	$\lvert S_{ab}\rvert$	C–Li	$\lvert S_{ab}\rvert$
$p_z{}^1 - p$	0.11	$s^1 - s$	0.22
$p_z{}^1 - p$	0.07	$s^{10} - p_z$	0.34
$p_z{}^9 - p$	0.12	$s^1 - p_z$	0.24
$p_z{}^9 - p$	0.06	$p^{10} - s$	0.12
$p_z{}^{10} - p$	0.02	$p^1 - s$	0.09
$p_z{}^{10} - p$	0.14	$p^9 - s$	0.13
$s^9 - p$	0.38		
$s^9 - s$	0.29		
$s^{10} - s$	0.27		

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(14) J. D. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7346 (1972).

carbanion three-center bond is important to the stabilization of di- and triaryl methyl complexes.

The INDO results further indicate that a σ interaction involving the s and p_z orbitals of the lithium atom and the combinations of ring carbon s and p_z orbitals which make up lower energy carbanion molecular orbitals is important. It is this interaction which is responsible for the positioning of the lithium atom closest to the carbon atom or atoms with the largest net atomic charge. If one views the complex as the result of a reaction between a B_2Li^+ and an Ar^{n-} species, the organic base can donate electron density to the B_2Li^+ acid *via* both the σ and the three-center bond.

The compatibility of the solid-state structural data obtained for the naphthalene dianion with the esr results for the naphthalene radical in solution is discussed in ref 14. There remains the apparent disagreement with the nmr results for fluorenyllithium of ref 8a. The proton chemical shifts for the fluorenyl carbanion are given in Table VIII. Both $FLi(DME)_n$ in DME and $FLi(THF)_n$ in THF are suggested to exist in solution as solvent-separated ion pairs.[15-17] This is consistent with the observation that the fluorenyl proton chemical shifts are nearly identical in these solvents. It is reasonable to expect that the 1:1 dimethoxyethane (DME) adduct in benzene will have the same structural configuration as the 2:1 quinuclidine adduct described here although in solution a rapid equilibrium will exist with the lithium atom going from the FC(1) to the FC(8) side of FC(9). The proton shifts for FLiDME in C_6D_6 and for $FLi(THF)_n$ in THF or $FLi(DME)_n$ in DME then represent the two extremes of contact and solvent-separated species. Unfortunately, a large solvent effect on the proton chemical shifts can be expected in benzene and this may be responsible for the unusual shifts observed for the coordinated DME and THF protons as well as for perturbation of the fluorenyl proton shifts.[18] Additional magnetic anisotropy effects due to the presence of the lithium atom are also neglected. The question that we wish to examine here is what effect one can expect on the proton chemical shifts due to differences in the charge distributions of the free and complexed fluorenyl carbanion. The approximation $\rho_{\text{nmr}} = \delta_{\text{benzene}}/k$ is used where δ_{benzene} is the proton chemical shift relative to benzene, $k = 10.7$, and the ρ = electron density at the carbon atom directly associated with the proton.[19] Charges for the isolated and contact ion pair fluorenyl carbanion were calculated by the CNDO techniques. The results are given in Table IX and demonstrate that the observed shifts are well within the range expected for the difference in charge distributions. It is also obvious that proton chemical shifts are not very sensitive to a difference of nearly 0.5 electron in the total ring charge in the fluorenyl carbanion. Although the excess number of variables in the nmr results does not permit a detailed analysis of the results in Table IX, it is interesting to note that the differences in proton chemical shifts more closely follow the differences in the proton charge densities than changes in the carbon charge densities. Any analysis of the carbanion charge distribution must obviously include both proton and carbon charge densities.[20] Lithium-7 chemical shifts can be expected to be more sensitive to the formation of contact or solvent-separated species; however, it is important that the comparison of Li^7 chemical shifts be made in the same solvent.

Table VIII. Proton Chemical Shifts for Fluorenyl Metal Systems (F = Fluorenyl)

Compound	Solvent	ν_1[a]	ν_2	ν_3	ν_4	ν_9
$FLi(DME)_n$[b]	DME	7.21	6.72	6.32	7.78	5.87
$FLi(THF)_n$[b]	THF	7.20	6.72	6.30	7.78	5.80
FLi·3THF[b]	C_6D_6	7.65	7.25	6.91	8.24	6.00
FLiDME[b]	C_6D_6	7.80	7.36	7.04	8.35	6.27
$FNa(THF)_n$[c]	THF	7.376	6.899	6.546	8.004	6.035
$FK(THF)_n$[c]	THF	7.272	6.808	6.542	7.865	5.893
$FRb(THF)_n$[c]	THF	7.247	6.806	6.441	7.815	5.884

[a] Chemical shifts downfield from TMS. [b] J. A. Dixon, *et al.*, *J. Amer. Chem. Soc.*, **87**, 1379 (1965). [c] R. H. Cox, *J. Phys. Chem.*, **73**, 2649 (1969).

Table IX. Fluorenyl Ring Atom Charges as Estimated by the Method of Ref 24 and CNDO II Calculations

	Solvent separated		Disolvated contact ion pair			
Atom	ρ_{CNDO}	ρ_{nmr}[a]	ρ_{CNDO}	ρ_{nmr}	$\Delta\rho_{\text{CNDO}}$	$\Delta\rho_{\text{nmr}}$
C_1	−0.10	−0.06	−0.05	−0.00	−0.05	−0.06
C_2	0.04	−0.07	0,02	−0.01	+0.02	−0.06
C_3	−0.11	−0.11	−0,06	−0.04	−0.05	−0.07
C_4	0.04	−0.02	0.02	+0.03	+0.02	−0.05
C_9	−0.26	−0.22	−0.18	−0.18	−0.08	−0.04
C_{10}	0.07		0.07		0.0	
C_{11}	−0.08		−0.05		−0.03	
C(1)H	−0.04		−0.01		−0.03	
C(2)H	−0.07		−0.03		−0.04	
C(3)H	−0.04		−0.02		−0.02	
C(4)H	−0.06		−0.02		−0.04	
C(9)H	−0.03		+0.02		−0.05	

[a] $\rho_{\text{nmr}} = \delta_{\text{benzene}}/10.7$ corrected for ring current in neighboring ring by $\delta_1 = 12.0(a^2/R^3)$: T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

Finally, we would point out that the bonding model proposed in this paper suggests that the point of closest approach of the metal ion to the carbanion can be expected to vary. The disolvated lithium atom is acting as a Lewis acid and accepts electron density from the ring *via* the three-center bond as previously described. If one forms a trisolvated lithium atom, the empty metal p orbital is no longer available and the bonding site will probably be determined by the σ bonding of the lithium sp^3 orbital to FC(9) or by the minimum in the electrostatic potential of the carbanion. The former mode would suggest a lithium position similar to that of one of the FC(9) protons in fluorene, while the latter would predict the lithium atom to be just inside the perimeter of the five-membered ring (Figure 3) of the fluorenyl carbanion as suggested by Dixon.[8a] This position is definitely expected for other alkali metals in that the formation of three-

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(15) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

(16) L. L. Chan and J. Smid, *ibid.*, **89**, 4549 (1967).

(17) T. Ellingsen and J. Smid, *J. Phys. Chem.*, 73, 2712 (1969).

(18) A. W. Langer, Esso Research Corp., private communication, 1971.

(19) For a discussion of this approximation, see T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(20) R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, 117 (1969).

center or σ bonds is unfavorable for Na, K, Rb, or Cs. A somewhat more difficult case to evaluate occurs when the lithium atom is coordinated to a base such as bipyridine or phenanthroline in which the possibility exists for the lithium atom to achieve saturation of its coordination sphere by delocalization of π electrons from the amine base to the lithium atom. The structure which is obtained may turn out to depend upon the relative electron affinity of the organic aromatic group compared to that of the bipyridine or phenanthroline base. Structural and spectroscopic investigations of the above types of systems are in progress.

The π-aromatic organolithium compounds are not the first examples of second row metal–ligand bonding which requires the use of an empty metal p orbital. In $[Be[N(CH_3)_2]_2]_3$,[21] the beryllium atom completes its electronic octet by a ligand → metal π bond. In fact, the above beryllium and lithium structures represent an extension of the principle stated over 20 years ago by Rundle, namely, if a metal, with more low-energy orbitals than valence electrons, is combined with atoms or groups with no unshared electron pairs, bonds are delocalized so as to make use of all the low-energy orbitals of the metal.[22,23]

[21] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 4426 (1969).

[22] R. E. Rundle, *ibid.*, **69**, 1327 (1947).

[23] R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949).

π Groups in Ion Pair Bonding. Stabilization of the Dianion of Naphthalene by Lithium Tetramethylethylenediamine

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Abstract: Bis[(tetramethylethylenediamine)lithium(I)] naphthalenide, $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$, has been synthesized and isolated from the reaction of 1,4-dihydronaphthalene, *n*-butyllithium, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in hexane. The structure of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ was determined at room temperature from three-dimensional X-ray data collected by counter methods. Refinement of the structure by least-squares techniques gave a final *R* factor on *F* of 0.059, based on 779 observations above background. The material crystallizes in the space group $C_{2h}{}^5$–$P2_1/c$ of the monoclinic system with two molecules in a cell of dimensions $a = 8.970$ (3), $b = 15.083$ (6), $c = 11.474$ (4) Å; $\beta = 129.5$ (1)°. The observed and calculated densities are 1.0 (1) and 1.04 g/cc, respectively. The crystallographic symmetry of the molecule is $C_i = \bar{1}$, so that only half of the naphthalene ring atoms, one lithium atom, and one TMEDA molecule are unique. The coordination sphere of the unique lithium atom contains two tertiary amine nitrogen atoms (Li–N = 2.11 (1) Å) and a portion of the unsaturated organic group. A perpendicular from a lithium atom to the mean plane of the naphthalenide carbon atoms intersects the plane at a point which is within a six-membered ring. Using the conventional numbering system for the parent molecule, naphthalene, this point is located on the perpendicular bisector of the C(1)–C(4) vector and closer to C(2) and C(3) than to C(9) and C(10). The location of the lithium atom is not consistent with the simple electrostatic considerations but is explicable in terms of the formation of a multicenter bond between a vacant lithium p orbital and the combination of ring-carbon-atom p orbitals which is derived from the highest occupied molecular orbital of the isolated carbanion. The point group symmetry of the naphthalene dianion should be the same as that of the first excited B_{2u} state of naphthalene and is found to be very nearly C_{2h} in this structure. The bond lengths in the naphthalenide fragment are close to what one would expect from the symmetry of the highest occupied molecular orbital of the dianion of naphthalene. The aromatic group is not planar with four atoms 0.15 Å off the mean plane of the group. INDO calculations made for the naphthalene radical monoanion utilizing the nonplanar geometry found for the naphthalenide ion in this structure are found to give a significantly improved fit to the experimental epr hyperfine coupling constants for the naphthalene monoanion.

It has been known for some time that aromatic hydrocarbons react with alkali metals to form mono- and dinegative ions.[1,2] The monoanions are free radicals with one electron in the lowest unoccupied π orbital[3] of the parent hydrocarbon so that further reduction to the dianion produces diamagnetic species with a pair of electrons in the same molecular orbital. The formation of the dianion of naphthalene with lithium as the reducing agent was first reported by Buschow and Hoijtink[4] and later by Smid.[5] These species were generated in THF solution using naphthalene and lithium metal and were not isolated as solids. The preparation of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ described below is the first example of the generation of the napthalene dianion using 1,4-dihydronaphthalene and *n*-butyllithium. The details of this reaction have not been fully examined at this time. We believe that the isolation of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ in crystalline form is the first reported example of the

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