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]

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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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isolation and characterization of a dialkali metal–naphthalene dianion compound in the solid state.

Our interest in this system was the result of several considerations. First, considerable structural data have been accumulated for transition metal complexes which contain unsaturated organic groups. It would seem useful to compare the structures of these compounds with corresponding structures of the representative elements in order to further evaluate the stereochemical effect of d orbitals in the transition metal systems. Second, the alkali metal–aromatic complexes are important reducing reagents as exemplified by the Birch reduction reaction, the synthesis of low-valent transition metal organometallic systems, and their catalytic properties in polymerization reactions. Little is known about the molecular nature of these reagents. Third, it has been recognized for some time[6–8] that the point group symmetry of a molecule in the first excited state will, with few exceptions, be that of the reduced species. Thus, the point group symmetry of the first excited state of naphthalene should be the same as that of the mono- or dianion of naphthalene. It is accordingly hoped that structural data such as that reported here will provide information not only about the carbanion but also about the excited state geometry of the parent organic molecule as well. Fourth, it has been pointed out[9] that the esr spectra of radical complexes of lithium are frequently anomalous when compared to the other alkali metal systems. The formation of a three-center bond[10] appears to be a factor in determining the structural properties of unsaturated complexes of lithium and may be important in explaining spectroscopic data. Additional structural data are needed to substantiate this possibility. In any event, since the same highest occupied molecular orbital of the carbanion is involved, it is to be expected that the structural results obtained for the dianion of naphthalene will be useful in the interpretation of the esr spectrum of the radical anion of naphthalene.[11,12]

Experimental Section

A 0.85-g (0.0065 mol) sample of 1,4-dihydronaphthalene was added to a 300-ml flask containing 200 of ml hexane and 1.5 g (0.013 mol) of *N,N,N′,N′*-tetramethylethylenediamine under a nitrogen atmosphere. A 10-ml (0.013 mol) sample of *n*-butyllithium in hexane was added to the flask *via* syringe. The resulting solution initially turned yellow and then over a period of 12 hr to a dark purple color. The flask was transferred to an inert atmosphere box and the crystalline product collected by filtration. After the crystals were washed with hexane and dried under vacuum, they were found to be suitable for single-crystal X-ray analysis without further purification.

Crystals for single-crystal X-ray analysis were sealed in thin-walled glass capillaries in an argon atmosphere because of the sensitivity of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ to oxygen and water. The crystals grew as dark purple needles and were oriented approximately along the c^* axis when mounted in the capillaries. Precession photographs showed that the crystals are monoclinic with absences for $0k0$, $k = 2n + 1$, and for $h0l$, $l = 2n + 1$, so that the space group is $P2_1/c$. The lattice parameters ($T = 23°$, $\lambda = 0.71069$ Å) determined from the least-squares refinement of 12 carefully centered peaks on a Picker four-circle diffractometer are $a = 8.970$ (3), $b = 15.083$ (6), $c = 11.474$ (4) Å; $\beta = 129.5$ (1)°. The calculated density for two molecules per unit cell is 1.04 g/cc^3. An estimation of 1.0 (1) g/cc for the density was obtained by the flotation method in a mixture of benzene and chlorobenzene. A more accurate measurement of the density could not be obtained due to the instability of the compound in various solvent mixtures.

Intensity data were measured using Mo Kα radiation on an automated Picker four-circle diffractometer equipped with a highly oriented graphite single-crystal monochromator. The crystal, an elongated parallelepiped of dimensions 0.50 × 0.25 × 0.20 mm, was oriented for data collection so that the c^* axis was coincident with the ϕ axis of the diffractometer. Several ω scans showed the typical full peak width at half-height to be approximately 0.12° indicating that the mosaicity was acceptably low for data collection. A survey of various peaks showed that a 2θ scan of 1.5° was sufficient to obtain all the peak intensity. A full form of data ($h\bar{k}l$) and ($\overline{hk}l$) was measured to $2\theta_{max} = 45°$, giving a total of 1739 reflections of which 1628 were unique.

Of the unique data, 779 reflections were considered observed using the criteria $I_{obsd} > 3\sigma_c(I)$ where $\sigma_c = [T_o + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$; 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. Only these observed reflections were used in the structure refinement. The remainder of the data collection details is the same as reported previously.[10]

Solution and Refinement of the Structure. The observed density suggested two molecules per unit cell so that the molecule must be located on a crystallographic inversion center. This means that only 14 nonhydrogen atoms needed to be located. The solution of the structure of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ was a textbook example of the use of direct methods (symbolic addition procedure) for structural solution and will not be discussed here. The scattering factor tables which were used and other details are given in ref 10. One cycle of full-matrix, least-squares refinement of the scale factor and E-map positional parameters using ORFLSD[13] gave a weighted R factor

$$R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2} = 0.178$$

After an additional cycle of varying positional parameters, the thermal parameters were varied isotropically along with the positional parameters. Three cycles resulted in isotropic convergence with a weighted R factor of 13.5%. Since no refinement of the hydrogen atom positional or thermal parameters was planned and no clear positions could be obtained from the difference Fourier, the theoretical hydrogen atom positions were based on known atom positions and hybridizations using HYGEN.[14] Each hydrogen atom was given an isotropic thermal parameter equal to that of its parent carbon atom and placed 1.02 Å from that atom. One more cycle of isotropic refinement of nonhydrogen atoms with hydrogen atom positions from HYGEN gave a weighted R factor of 9.6%. Further refinement of positional and thermal parameters after conversion from isotropic to anisotropic thermal parameters led to final R factors.

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.059$$

$$R_2 = 0.057$$

The estimated standard deviation of an observation of unit weight was 2.54. There were no peaks higher than 0.2 e/Å^3 on the last difference Fourier map which was calculated.

The entire refinement to this point had been done using unit weights. A test of unit weights revealed no systematic variation of $w(F_o - F_c)^2$ with the magnitude of the structure factors or $\sin\theta/\lambda$. For comparison, new weights were assigned on the basis of counting statistics. Two cycles of anisotropic refinement led to converged values for the R factors of $R_1 = 0.070$ and $R_2 = 0.056$. A test of the counting statistics weighting scheme showed no systematic variation of $w(F_o - F_c)^2$ with the magnitude of the structure factors but a marked systematic decrease in $w(F_o - F_c)^2$ with respect to increasing $\sin\theta/\lambda$. On the basis of these results, it was decided that unit weights would be adequate for these data.

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Table I. Positional Parameters for the Nonhydrogen Atoms in $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$

Atom	x	y	z
RC(1)	−0.2751 (8)	0.5685 (4)	0.0946 (7)
RC(2)	−0.1779 (8)	0.5484 (4)	0.2511 (7)
RC(3)	−0.2427 (9)	0.4825 (5)	0.2872 (5)
RC(4)	−0.4102 (8)	0.4342 (4)	0.1711 (7)
RC(5)	−0.5347 (7)	0.4651 (3)	0.0207 (6)
N(1)	−0.2312 (6)	0.3197 (3)	0.0000 (5)
N(1)C(1)	−0.2965 (11)	0.2455 (5)	0.0382 (8)
N(1)C(2)	−0.3825 (10)	0.3388 (5)	−0.1600 (8)
C(1)	−0.0493 (9)	0.3004 (4)	0.0327 (8)
C(2)	0.1195 (9)	0.3069 (5)	0.1926 (7)
N(2)	0.1234 (6)	0.3871 (3)	0.2685 (5)
N(2)C(1)	0.2088 (1)	0.4595 (5)	0.2452 (10)
N(2)C(2)	0.2297 (10)	0.3710 (5)	0.4256 (8)
Li	−0.1719 (13)	0.4221 (6)	0.1475 (11)

Table II. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
RC(1)	0.0194 (14)	0.0039 (3)	0.0173 (11)	0.0001 (6)	0.0115 (11)	−0.0006 (5)
RC(2)	0.0192 (14)	0.0046 (4)	0.0142 (11)	0.0014 (6)	0.0051 (11)	−0.0028 (5)
RC(3)	0.0284 (18)	0.0065 (4)	0.0099 (9)	0.0054 (7)	0.0092 (12)	0.0007 (5)
RC(4)	0.0263 (16)	0.0045 (3)	0.0140 (10)	0.0034 (6)	0.0132 (11)	0.0020 (5)
RC(5)	0.0173 (13)	0.0033 (3)	0.0111 (8)	0.0020 (5)	0.0091 (9)	−0.0001 (4)
N(1)	0.0204 (12)	0.0047 (3)	0.0151 (8)	0.0005 (5)	0.0114 (9)	−0.0005 (4)
N(1)C(1)	0.0502 (25)	0.0067 (4)	0.0260 (14)	−0.0052 (9)	0.0265 (17)	−0.0024 (7)
N(1)C(2)	0.0378 (21)	0.0074 (5)	0.0195 (12)	0.0013 (8)	0.0171 (14)	−0.0004 (6)
C(1)	0.0287 (19)	0.0071 (4)	0.0236 (13)	0.0018 (7)	0.0172 (13)	−0.0019 (6)
C(2)	0.0259 (18)	0.0085 (5)	0.0184 (12)	0.0058 (8)	0.0121 (13)	0.0010 (6)
N(2)	0.0187 (12)	0.0053 (3)	0.0149 (8)	0.0012 (5)	0.0095 (9)	0.0007 (4)
N(2)C(1)	0.0384 (23)	0.0085 (5)	0.0358 (19)	−0.0005 (9)	0.0253 (19)	−0.0017 (8)
N(2)C(2)	0.0328 (21)	0.0120 (6)	0.0163 (12)	0.0081 (9)	0.0123 (14)	0.0017 (7)
Li	0.0198 (22)	0.0040 (5)	0.0152 (14)	0.0010 (9)	0.0100 (16)	−0.0011 (7)

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

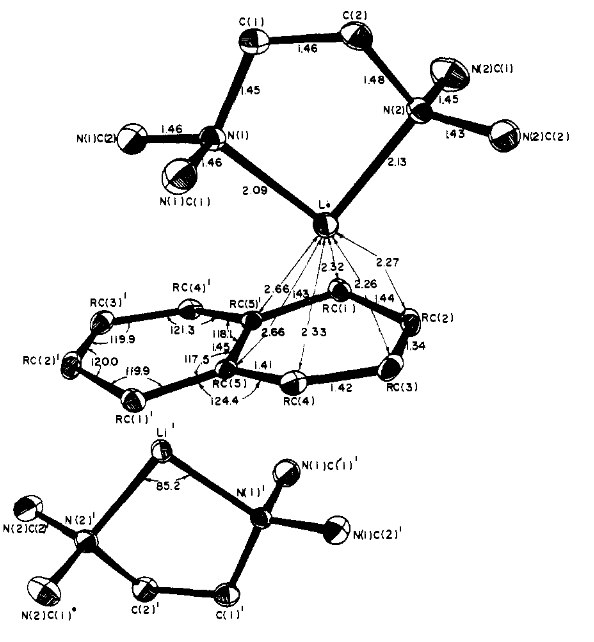

Figure 1. The molecular geometry of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$.

The molecular structure for $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ is shown in Figure 1. The positional parameters of the primed atoms appearing in Figure 1 and the tables are related to those of the corresponding unprimed atoms as follows: $(x', y', z') = (-1 - x, 1 - y, -z)$. Final positional and thermal parameters for all nonhydrogen atoms are given in Tables I and II. Bond distances and angles and their errors appear in Tables III and IV. Table V gives the best weighted least-squares planes for the naphthalene dianion.[15]

Discussion

Lithium Atom Environment. The structure of $Li\{[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$ (Figure 1) consists of the $C_{10}H_8$ moiety bound to two lithium atoms, each of which is coordinated to an *N,N,N′,N′*-tetramethylethylenediamine group. The molecule is situated on an inversion center so that only half of the naphthalene ring atoms, one lithium atom, and one TMEDA molecule are unique. The coordination sphere of the lithium atom contains two tertiary amine nitrogen atoms and one unsaturated organic group as in benzyllithium triethylenediamine,[16a] fluorenyllithium bisquinuclidine,[10] and triphenylmethyllithium tetramethylethylenediamine.[16b]

Table III. Interatomic Distances (Å) for the Nonhydrogen Atoms[a] in $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$

Atoms	Distance	Atoms	Distance
Li–N(1)	2.094 (10)	RC(4)–RC(5)	1.412 (7)
Li–N(2)	2.133 (9)	RC(5)–RC(5)′	1.447 (10)
Li–RC(1)	2.321 (10)	N(1)–N(1)C(1)	1.455 (8)
Li–RC(2)	2.265 (10)	N(1)–N(1)C(2)	1.459 (7)
Li–RC(3)	2.257 (11)	N(1)–C(1)	1.453 (7)
Li–RC(4)	2.327 (11)	C(1)–C(2)	1.462 (9)
RC(1)–RC(2)	1.444 (8)	N(2)–C(2)	1.478 (8)
RC(1)–RC(5)′	1.432 (7)	N(2)–N(2)C(1)	1.453 (8)
RC(2)–RC(3)	1.343 (8)	N(2)–N(2)C(2)	1.426 (8)
RC(3)–RC(4)	1.422 (8)		

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

The average lithium–nitrogen bond length of 2.11 (1) Å is slightly longer than the lithium–nitrogen bond lengths of the other amine-solvated organolithium compounds studied and, based on the previously discussed correlation between Li–N bond lengths and

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[15] The observed and calculated structure factors and the calculated positions and assigned isotropic thermal parameters for the hydrogen atoms 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-72-7346. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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Table IV. Bond Angles (deg) for the Nonhydrogen Atoms in $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$

Atoms	Angle	Atoms	Angle
N(1)–Li–N(2)	85.2 (4)[a]	Li–N(1)–N(1)C(1)	105.5 (5)
RC(1)–Li–RC(2)	36.7 (2)	Li–N(1)–N(1)C(2)	115.3 (5)
RC(1)–Li–RC(4)	73.3 (3)	C(1)–N(1)–N(1)C(1)	111.6 (5)
RC(2)–Li–RC(3)	34.5 (3)	C(1)–N(1)–N(1)C(2)	111.1 (5)
RC(3)–Li–RC(4)	36.1 (3)	N(1)C(1)–N(1)–N(1)C(2)	107.5 (5)
RC(5)′–RC(1)–RC(2)	119.9 (5)	N(1)–C(1)–C(2)	114.1 (6)
RC(1)–RC(2)–RC(3)	120.0 (5)	C(1)–C(2)–N(2)	114.4 (5)
RC(2)–RC(3)–RC(4)	119.9 (5)	Li–N(2)–C(2)	105.3 (4)
RC(3)–RC(4)–RC(5)	121.3 (5)	Li–N(2)–N(2)C(1)	106.0 (5)
RC(4)–RC(5)–RC(5)′	118.1 (6)	Li–N(2)–N(2)C(2)	114.9 (5)
RC(4)–RC(5)–RC(1)′	124.4 (5)	C(2)–N(2)–N(2)C(1)	108.9 (5)
RC(5)–RC(5)′–RC(1)	117.5 (6)	C(2)–N(2)–N(2)C(2)	110.6 (5)
Li–N(1)–C(1)	105.6 (4)	N(2)C(1)–N(2)–N(2)C(2)	110.7 (6)

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

Table V. Best Weighted Least-Squares Planes for $\{Li[(CH_3)_2N(CH_2)_2N(CH_2)_2]\}_2C_{10}H_8$

Plane	Atoms in plane	Equation of plane[a]
1	RC(1), RC(2), RC(3), RC(4), RC(5), RC(1)′, RC(2)′, RC(3)′, RC(4)′, RC(5)′	$0.7197x - 0.6773y - 0.1523z + 8.3359 = 0$
2	RC(2), RC(3), RC(5), RC(2)′, RC(3)′, RC(5)′	$0.7294x - 0.6719y - 0.1277z + 8.3392 = 0$
3	RC(1), RC(2), RC(3), RC(4)	$0.7539x - 0.6568y - 0.0034z + 8.0206 = 0$
4	RC(1), RC(4), RC(5), RC(5)′	$0.6867x - 0.6841y - 0.2456z + 8.2394 = 0$

	Deviations of atoms from planes, Å			
Atom	Plane 1	Plane 2	Plane 3	Plane 4
RC(1)	0.127 (8)	0.166 (8)	0.003 (8)	−0.002 (7)
RC(2)	−0.074 (8)	−0.005 (8)	−0.007 (8)	
RC(3)	−0.057 (8)	0.006 (8)	0.008 (9)	
RC(4)	0.121 (8)	0.149 (8)	−0.004 (8)	0.002 (7)
RC(5)	−0.004 (6)	−0.007 (6)		−0.002 (6)
RC(1)′	−0.127 (8)	−0.166 (8)		
RC(2)′	0.074 (8)	0.005 (8)		
RC(3)′	0.057 (8)	−0.006 (8)		
RC(4)′	−0.121 (8)	−0.149 (8)		
RC(5)′	0.004 (6)	0.007 (6)		0.002 (6)
Li	1.940 (12)	1.984 (12)	1.859 (12)	1.765 (12)

The dihedral angle between planes 3 and 4 is 14.5°

[a] The orthogonal unit cell vectors x, y, z are related to the monoclinic vectors a, b, c as follows: $(x, y, z) = (a + c \cos \beta, b, c \sin \beta)$.

carbanion stabilities,[16b] suggests that the carbanion stability of the naphthalene dianion is less than that of the benzyl, fluorenyl, or triphenylmethyl carbanions. The N–Li–N angle of 85.2° agrees with the N–Li–N angles in ethylenediamine-type lithium compounds.[16b] The somewhat shortened C(1)–C(2) ethylene carbon–carbon bond length (1.46 Å) in the TMEDA group may mean that there is some disorder of the group. This disorder is probably compensated for by anisotropic thermal motion and is small in comparison to the disorder in the TMEDA group of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$.[16b] The TMEDA group plays an important role in the crystal packing (Figure 2) and appears to be more constrained then it is in the triphenyl methyllithium structure.

The lithium cation assumes a symmetrical position with respect to the ring. It is 2.26 Å from RC(3), 2.27 Å from RC(2), 2.32 Å from RC(1), 2.33 Å from RC(4), and 2.66 Å from both RC(5) and RC(5)′. These values show that it is not located over the center of the ring but is shifted toward the outside RC(2)–RC(3) bond. An examination of a CNDO molecular orbital calculation for the naphthalene dianion produces some interesting results (Figure 3). The gross atomic charges from the CNDO treatment suggest that there are positive charges at the RC(5) and RC(5)′ (+0.072) positions while all the other atoms have negative charge densities with the greatest negative charge densities (−0.256) at RC(1) and RC(4). The hydrogen atoms RC(2)H and RC(3)H also have considerable negative density (−0.132). At first glance, the positive charges at RC(5) and RC(5)′ combined with the negative charges at all other positions would appear to account for the shifting of the lithium cation away from the center of the naphthalene ring toward the RC(2)-RC(3) bond. However, a calculation of the potential energy surface 2.0 Å above the mean plane of the anion using the atomic charges given in Figure 3 gives a result very similar to that given in ref 9 with a shallow double minimum in the electrostatic potential located near RC(5) and RC(5)′. The electrostatic model does not therefore correctly predict the stereochemistry of the complex.

INDO[17] molecular orbital calculations suggest that as in fluorenyl- and benzyllithium $(base)_2$[10] compounds, both π and σ bonding to the aromatic ring are important. More specifically, we note that the molecular orbitals which have the largest amount of lithium

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(17) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

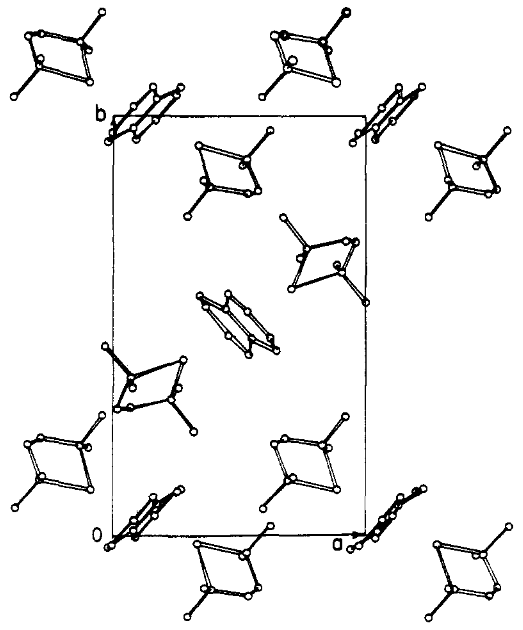


Figure 2. The *ab* projection of the unit cell of $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{10}H_8$.

character have small contributions from RC(5) and RC(5)′. For example, the symmetries of the two highest occupied molecular orbitals of the dianion are shown below. These are made up of carbon p_z orbitals with the coefficients for RC(5) p_z and RC(5)′ p_z being zero.

The symmetries of these carbanion molecular orbitals are retained in the two HOMO's of the metal complex. As in fluorenyllithium bisquinuclidine[10] and benzyllithium triethylenediamine,[16a] the lithium atom is approximately located over a node in the HOMO of the organic anion (structure to the left above). Thus optimizing the use of the Li p orbital which is parallel to the mean carbanion plane, the results of INDO calculations show that bonding between the HOMO carbanion molecular orbitals and lithium p orbital is substantial and probably responsible for the positioning of the lithium atoms to the outside of the phenyl rings rather than over the minima of the electrostatic potential. This is in agreement with the interpretation given previously[11] that the geometry of the metal-unsaturated organic group complex is primarily determined by the interaction of the empty lithium orbital(s) with the HOMO of the free carbanion in these compounds.

Naphthalenide Ion. The naphthalenide geometry is close to what one would predict from the symmetry of the HOMO of the dianion of naphthalene. In the naphthalene molecule, Cruickshank[18] has reported bond lengths of 1.364 (5) Å for RC(1)-RC(2), 1.415 (5) Å for RC(2)-RC(3), 1.421 (5) Å for RC(1)-RC(5)′, and 1.418 Å for RC(5)-RC(5)′. In the dianion, the contribution from the HOMO to the RC(1)-RC(2) bond is antibonding and that bond length is increased 0.07 Å to an average value of 1.433 (8) Å. The node in the HOMO at RC(5)-RC(5)′ means that little change should be expected in the RC(4)-RC(5) and RC(5)-RC(5)′ bond lengths. The 1.447 (10) Å bond length observed for RC(5)′-RC(5) is therefore somewhat longer than anticipated. The RC(2)-RC(3) bond length is decreased 0.08 Å from 1.415 (5) to 1.343 (8) Å in agreement with the fact that the contribution to this bond by the HOMO in the dianion is predicted to be strongly bonding. Most notable in the structure of the dianion is the fact that the naphthalene ring system is no longer planar with the atoms RC(1), RC(4), and RC(1)′, RC(4)′, 0.15 Å on either side of plane 2 of Table V.

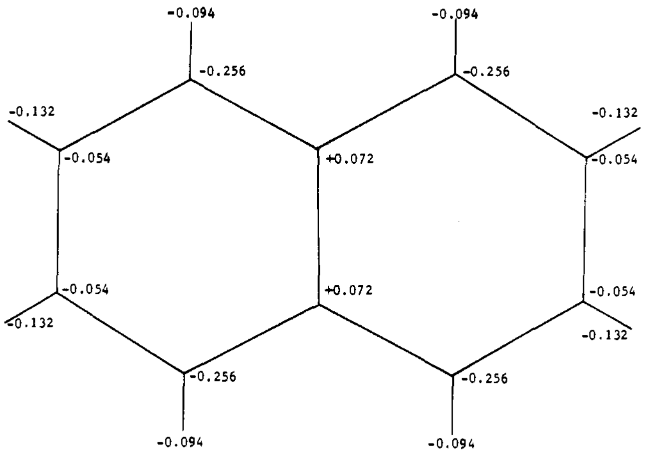
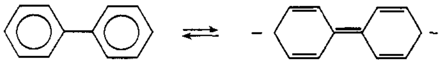
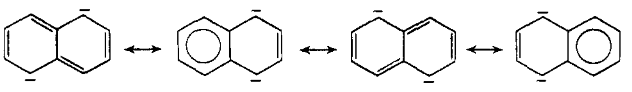


Figure 3. Gross atomic charges from the CNDO molecular orbital calculation for the naphthalene dianion.

A rule[7,8] for predicting the point group symmetry of excited states of molecules is as follows. The first excited state of a molecule containing *n* electrons should belong to the same point group as the ground state of a similar molecule having $n + 1$ or $n + 2$ electrons. The extra one or two electrons are assumed to be in that molecular orbital which becomes occupied in the excited state. Adding electrons to a planar aromatic ring should cause some atoms to bend out of the plane. For example, the reduction of benzene would give the dianion of cyclohexadiene. Occasionally, a predominant resonance structure is indicated for a reduced aromatic molecule which should resemble the excited state most closely.



However, it is to be expected that, in most aromatic hydrocarbons, a single resonance structure will not suffice (see below).



The results of this study would indicate that the point group symmetry of the first excited state of naphthalene should be C_{2h} with a mirror plane perpendicular to the RC(2)-RC(3) and RC(5)-RC(5)′ bonds.[18a]

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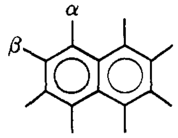
[18] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960).

[18a] Note Added in Proof. Recently theoretical structures have been predicted for the first two excited singlet states of naphthalene (planar geometries only). The reader is referred to Y. Fujimura, H. Yamaguchi, and T. Nakajima, *Bull. Chem. Soc. Jap.*, **45**, 384 (1972).

Several attempts have been made to fit the hyperfine coupling constants of alkali metal–organic radical anion systems by varying structural parameters of the metal complex.[12,19] The results obtained by Pedersen and Griffin[12] are given in Table VI along with observed values reported by Hirota.[11] The striking point is the greatly improved fit obtained for the hyperfine coupling constant of the β proton using the nonplanar structure of the carbanion as found in the structure of [LiTMEDA]$_2$ naphthalene. Ring carbon bond lengths are not nearly as important as evidenced by the results in column 1 which are very similar to those obtained by Pedersen and Griffin for the naphthalene (O) geometry. It is interesting that including the lithium atom in the position observed in the crystal structure algebraically increases the magnitudes of the hyperfine coupling constants of the α and β protons in the direction suggested by the observed data. The implications of the above to reported esr data for other radical anions are being investigated. It is also reassuring that structural data obtained in the solid state give reasonable results when applied to the interpretation of solution spectra. The bond lengths in the radical anion of naphthalene are probably intermediate between those of the naphthalene dianion and the naphthalene molecule. The angular distortion of the ring from planarity may, however, be similar in the radical and dianion since angular deformations are of lower energy. An additional complication should be mentioned here, namely, that the angular deformation of the carbanion in the contact ion pair may not be the same as in the solvent separated ion pair.

Table VI



	INDO hyperfine coupling constants				
	Calcd				
	Free anion		Complex		Obsd[a]
	b	*c*	*c*	*d*	
Li			0.19	0.22	0.1–0.4
α	−5.3	−5.8	−5.5	−5.3	(−)4.9
β	−0.88	1.60	1.72	−0.86	1.83

[a] N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968). [b] Assuming planar D_{2h} symmetry, with bond lengths as determined in the crystal structure of [LiTMEDA]$_2$ naphthalene and C–H distances of 1.08 Å. [c] Naphthalene geometry as observed in the crystal structure of [LiTMEDA]$_2$ naphthalene and C–H distances of 1.08 Å. [d] L. Pedersen and R. G. Griffin, *Chem. Phys. Lett.*, **5**, 373 (1970).

A calculation was carried out on the puckered naphthalene monoanion which suggests that the ^{13}C hyperfine coupling constants are much more sensitive to the position of the Li atom than the hydrogen atom hyperfine coupling constants. In the naphthalene monoanion, a coupling constant of 4.3 G was calculated for RC(5) and RC(5)′ while in the metal complex, $C_{10}H_8Li(NH_3)_2$, the corresponding hyperfine coupling constant is 0.26 G. It would appear that ^{13}C nmr and esr investigations may be a useful method of excluding certain structural possibilities in solution.

Acknowledgment. The authors gratefully acknowledge the generous support of the Advanced Projects Research Agency under Contract No. HC 15-67C0221 and the National Science Foundation.

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(19) G. W. Canters, C. Corvaja, and E. de Boer, *J. Chem. Phys.*, **54**, 3026 (1971).

Heat of Binding of Dinitrogen and Related Ligands to $[Ru(NH_3)_5H_2O]^{2+}$

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Abstract: The ΔH values for the reaction of $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5H_2O]^{3+}$ with ligands ranging from σ donors to π acceptors were measured by calorimetric techniques. The $[Ru(NH_3)_5H_2O]^{3+}$ ion binds more strongly to σ donor ligands while $[Ru(NH_3)_5H_2O]^{2+}$ forms more stable complexes with π-acceptor ligands. The replacement of one NH_3 by H_2O on each of the Ru atoms in $[Ru(NH_3)_5]_2N_2^{4+}$ decreases the ΔH of binding of the N_2 molecule by 6 kcal/mol. The reaction of $[Ru(NH_3)_5CO]^{2+}$ with a tenfold excess of Ce(IV) results in the oxidation of the bound CO to CO_2.

The $[Ru(NH_3)_5H_2O]^{2+}$ ion can coordinate a wide variety of ligands in place of the H_2O molecule. Stable and well-defined complexes range from ligands which are completely σ-donating (NH_3) to those ligands which are considered as weakly σ-donating and very likely strongly π-accepting (N_2, CO, etc.). The latter complexes have been studied recently[1] and, based primarily on the interpretation of infrared spectral data, the bonding to the unique ligand is thought to be best described as metal to ligand π-bonding, with perhaps a small degree of σ-bonding.

Although this explanation is reasonable, it appeared desirable to test these conclusions using an independent approach in which some property related to metal–ligand bonding is measured as the ligand char-

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(1) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).