and 1,10-phenanthroline to 56° yields rapid and nearly quantitative formations of $XRe(CO)_3(phen)$ as identified by ir and uv-visible spectra compared to authentic samples of the product. The $XRe(CO)_3(phen)$ is sparingly soluble in benzene and crystallizes from solution upon cooling from 56 to 25°. The typical procedure for quantitative measure of the substitution rate is given by the following: 0.0007 g of $ClRe(CO)_3(t\text{-}4\text{-stpy})_2$ and 0.0564 g of 1,10-phenanthroline were dissolved in 3.0 ml CH_2Cl_2. The solution was placed in a stoppered 1.00-cm path length cuvette and placed in the Cary 17 cell holder and thermostated to 56°. The optical density increase at 450 nm was followed as a function of thermolysis time. An isosbestic point is found at ~398 nm and about 15% conversion to $ClRe(CO)_3(phen)$ obtains in about 2 hr. The molar extinction coefficient for the product at 450 nm at 60° in CH_2Cl_2 is 940 l. mol^{-1} cm^{-1} determined from an authentic sample.

Acknowledgment. We thank the National Science Foundation and the National Aeronautics and Space Administration for support of this research. L.P. thanks the Agency for International Development, United States Department of State, for financial support.

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Unsaturated Organometallic Compounds of the Main Group Elements. The Isolation and Structural Properties of Bis[(tetramethylethylenediamine)lithium(I)] Anthracenide

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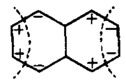
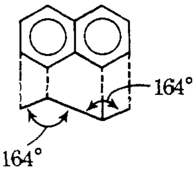
Abstract: Bis[(tetramethylethylenediamine)lithium(I)] anthracenide, $\{Li[(CH_3)_2N(CH_2)_2N(CH_3)_2]\}_2C_{14}H_{10}$, has been synthesized from 9,10-dihydroanthracene and *n*-butyllithium tetramethylethylenediamine and the molecular structure determined by single-crystal X-ray structural studies. The anthracenide group in this molecule exhibits structural distortions from the neutral anthracene molecular geometry which are consistent with the symmetry properties of the highest unoccupied molecular orbital of the anthracene molecule. In particular, a significantly nonplanar geometry is observed in keeping with a substantial antiaromatic character in the anthracenide fragment. The greater delocalization possible in anthracene compared to that for naphthalene results in a correspondingly smaller change in the anthracene molecular bond lengths in going from the neutral anthracene to the lithium anthracenide complex. One of the two lithium atoms is located over the central six-membered ring and the other is positioned on the opposite side of the molecule over one of the outer six-membered rings. The configuration for the lithium atom over the outer six-membered ring of the anthracene group is almost identical with that of the lithium atom with respect to the naphthalene fragment in bis[(tetramethylethylenediamine)lithium(I)] naphthalenide. The distances of the lithium atoms from the anthracene ring planes are 2.053 (5) and 1.994 (5) Å. The three-dimensional structure of bis[(tetramethylethylenediamine)lithium(I)] anthracenide was determined from 2462 single-crystal X-ray diffractometer data. The compound crystallizes in the monoclinic space group, $P2_1/c$ with lattice parameters (t = 23°) of a = 8.44 (1) Å, b = 17.43 (2) Å, c = 18.17 (2) Å, β = 91.5 (5)°. The calculated density is 1.06 g cm^{-3} for Z = 4. Least-squares refinement gave a weighted final agreement factor of 0.066.

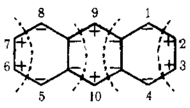
A recent study[1] of the molecular stereochemistry of bis[(tetramethylethylenediamine)lithium(I)] naphthalenide revealed a number of interesting points. The carbanion geometry was found to be consistent with the symmetry of the highest occupied molecular orbital (HOMO) of the carbanion molecule (below), with an increase in the C(1)-C(2) bond length of 0.07 Å and a corresponding decrease in the C(2)-C(3) bond length of 0.08 Å on the formation of the dianion. The naphthalenide dianion is a 4n π antiaromatic[2] system and the C(2)-C(3) bond length of 1.343 (8) Å, which is the value expected for a localized double bond as



well as the nonplanar character of the naphthalenide ring system (below), are significant. It was also shown that INDO open shell calculations for a *nonplanar* radical monoanion of naphthalene gave a significantly better fit to the observed hyperfine coupling constants. In particular, the calculated value for the coupling constant for C(2)H was +1.72, which can be compared with the observed value of $|1.83|$[3] and the calculated value of −0.88 for the planar monoanion.[4]



We were interested in extending the above observations to an unsaturated hydrocarbon in which (1) there was greater delocalization and for which (2) there was some ambiguity in the possible binding site of the lithium atom. A system which has been extensively studied and which meets the above requirements is anthracene. The symmetry of the HOMO orbital (made up of carbon $2p_z$ orbitals) of the anthracene carbanion as given by Hückel and INDO calculations is shown below. The sign of the molecular orbital at the centroid of the molecule is taken from the results of INDO calculations.[5]

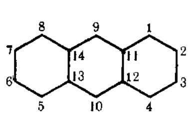


Previous studies[6-8] have suggested the following sequential rules in predicting the position(s) of the lithium atom(s) in disolvated lithium carbanion complexes: (1) the lithium atom will be located on a nodal surface of the HOMO; (2) the lithium atom(s) will be located near the minimum in the electrostatic potential of the anion, usually interacting most strongly with the carbon atom(s) of the carbanion which have the largest contribution to the highest occupied molecular orbital; (3) for monoanions, the LiB_2 fragment will be oriented in such a way that the LiB_2 plane is nearly coplanar with the nodal surface and in an allylic configuration with respect to two 1,3 carbon atoms of the carbanion.

The two atoms with the largest coefficients in the HOMO for the anthracenyl dianion are C(9) and C(10). Following (1) above, one lithium atom should therefore be most closely associated with these two carbon atoms. (2) suggests that if one lithium atom is located over the central six-membered ring in anthracene, it will be slightly displaced from a position over the center to one side of this ring, so that it lies on a nodal surface. A number of possibilities exist for the second lithium atom: (a) the second lithium atom could be on the opposite side of the central six-membered ring; (b) the second largest atomic coefficients are for C(1), C(4), C(5), and C(8), so that the second lithium atom could be in close proximity to either the pair C(1)-C(4) or C(5)-C(8); (c) another possible combination which would make the lithium atoms equivalent would be for the lithium atoms to be located near the pairs C(1)-C(9) and C(5)-C(10) (or C(8)-C(9) and C(4)-C(10)).

In this paper, the actual configuration observed for $[LiTMED]_2$(anthracenide) (TMED = tetramethylethylenediamine), the effect of carbanion formation on the anthracene geometry and the possible effect of the structural changes associated with reduction of the anthracene molecule upon the hyperfine coupling constants of the anthracene monoanion are presented.

Table I. Atomic Coordinates for the Nonhydrogen Atoms of $[LiTMED]_2C_{14}H_{10}$



	x	y	z
C(1)	−0.1072 (4)	0.0456 (2)	0.3829 (2)
C(2)	−0.1604 (5)	0.0727 (3)	0.4513 (2)
C(3)	−0.2574 (5)	0.1354 (3)	0.4524 (2)
C(4)	−0.3027 (4)	0.1718 (2)	0.3859 (2)
C(5)	−0.2975 (5)	0.1857 (2)	0.1114 (2)
C(6)	−0.2415 (6)	0.1581 (3)	0.0441 (3)
C(7)	−0.1494 (6)	0.0946 (3)	0.0432 (2)
C(8)	−0.1085 (4)	0.0568 (3)	0.1085 (2)
C(9)	−0.1348 (3)	0.0421 (2)	0.2449 (2)
C(10)	−0.3276 (3)	0.1695 (2)	0.2477 (2)
C(11)	−0.1651 (3)	0.0747 (2)	0.3147 (2)
C(12)	−0.2677 (3)	0.1414 (2)	0.3167 (2)
C(13)	−0.2636 (4)	0.1482 (2)	0.1785 (2)
C(14)	−0.1646 (3)	0.0817 (2)	0.1768 (2)
Li(2)	−0.0213 (6)	0.1733 (3)	0.4066 (3)
Li(1)	−0.4122 (6)	0.0429 (3)	0.2339 (3)
A1C(1)	−0.6580 (5)	0.0763 (3)	0.1142 (3)
A1C(2)	−0.4949 (5)	−0.0302 (3)	0.0990 (2)
A1C(3)	−0.5897 (7)	0.0025 (3)	0.3618 (3)
A1C(4)	−0.4212 (5)	−0.0967 (3)	0.3277 (3)
A1C(5)	−0.6498 (5)	−0.0702 (3)	0.2534 (3)
A1C(6)	−0.6960 (5)	−0.0329 (3)	0.1899 (2)
A1N(2)	−0.5803 (3)	0.0138 (2)	0.1534 (2)
A1N(1)	−0.5270 (3)	−0.0372 (2)	0.3008 (2)
A2C(1)	0.1098 (4)	0.2211 (3)	0.5613 (2)
A2C(2)	0.2711 (5)	0.1466 (3)	0.4837 (2)
A2C(3)	0.1310 (5)	0.2166 (2)	0.2611 (2)
A2C(4)	−0.0177 (5)	0.3108 (2)	0.3244 (2)
A2C(5)	0.2386 (4)	0.2726 (2)	0.3723 (2)
A2C(6)	0.2175 (4)	0.2784 (2)	0.4589 (2)
A2N(1)	0.1542 (3)	0.2077 (2)	0.4850 (1)
A2N(2)	0.0932 (3)	0.2477 (2)	0.3337 (1)

Table II. Anthracene Hydrogen Atom Positional and Isotropic Thermal Parameters in $[LiTMED]_2C_{14}H_{10}$

	x	y	z	B, Å
H(1)	−0.041 (4)	0.001 (2)	0.380 (2)	4.6 (8)
H(2)	−0.121 (4)	0.047 (2)	0.496 (2)	5.3 (9)
H(3)	−0.297 (3)	0.156 (2)	0.497 (2)	4.7 (8)
H(4)	−0.363 (3)	0.219 (2)	0.388 (1)	3.2 (7)
H(5)	−0.370 (4)	0.228 (2)	0.114 (2)	7.0 (11)
H(6)	−0.266 (4)	0.183 (2)	0.005 (2)	5.6 (10)
H(7)	−0.107 (4)	0.079 (2)	−0.001 (2)	7.0 (11)
H(8)	−0.041 (4)	0.012 (2)	0.108 (2)	4.7 (8)
H(9)	−0.073 (4)	−0.005 (2)	0.244 (2)	3.0 (7)
H(10)	−0.398 (4)	0.212 (2)	0.249 (2)	3.8 (8)

Experimental Section

An 0.013 mol sample of 9,10-dihydroanthracene was added to 100 ml of dry benzene and 3.0 g of *N,N,N′,N′*-tetramethylethylenediamine under a nitrogen atmosphere. A 20-ml (0.026 mol) sample of *n*-butyllithium in hexane was added to the flask via syringe. The solution turned a dark purple indicating formating of the anthracene dianion. The reaction was allowed to set 12 hr and then transferred to a drybox containing a helium atmosphere. Evaporation of the solvent left a maroon colored solid which gave good crystals after recrystallization from benzene. Crystals as large as 5 × 5 × 3 mm could be grown by slow evaporation of solvent.

Crystals for single-crystal X-ray analysis were sealed in thin-walled glass capillaries in a helium atmosphere because of the sensitivity of the anthracene dianion to oxygen and water. Precession photographs showed that the crystals are monoclinic with systematic absences on $0k0$ for $k = 2n + 1$ and on $h0l$ for $l = 2n + 1$, uniquely determining the space group $P2_1/c$. Least-squares refinement of the $(\sin \theta/\lambda)^2$ values of 12 reflections gave lattice parameters (t = 23°): a = 8.44 (1) Å, b = 17.43 (2) Å, c = 18.17 (2) Å, β = 91.55°, and ρ_{calc} = 1.06 g cm^{-3} with Z = 4 molecules.

Table III. Anisotropic Temperature Factors for the Nonhydrogen Atoms of $[\mathrm{LiTMED}]_2\mathrm{C}_{14}\mathrm{H}_{10}$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0171 (7)	0.0034 (2)	0.0034 (2)	−0.0002 (3)	−0.0007 (2)	0.0003 (1)
C(2)	0.0195 (7)	0.0045 (2)	0.0032 (2)	−0.0014 (3)	−0.0006 (3)	0.0005 (1)
C(3)	0.0182 (7)	0.0055 (2)	0.0028 (2)	−0.0024 (3)	0.0019 (3)	0.0007 (2)
C(4)	0.0145 (6)	0.0036 (2)	0.0033 (2)	0.0000 (3)	0.0003 (2)	−0.0005 (1)
C(5)	0.0209 (8)	0.0039 (2)	0.0040 (2)	−0.0022 (3)	−0.0018 (3)	0.0006 (1)
C(6)	0.0262 (9)	0.0059 (2)	0.0031 (2)	−0.0043 (4)	−0.0020 (3)	0.0009 (2)
C(7)	0.0217 (8)	0.0064 (3)	0.0030 (2)	−0.0041 (4)	0.0008 (3)	−0.0005 (2)
C(8)	0.0148 (6)	0.0050 (2)	0.0033 (2)	−0.0015 (3)	0.0002 (3)	−0.0004 (1)
C(9)	0.0116 (5)	0.0032 (1)	0.0035 (1)	0.0003 (2)	0.0000 (2)	−0.0002 (1)
C(10)	0.0127 (5)	0.0029 (1)	0.0039 (1)	0.0009 (2)	−0.0009 (2)	−0.0001 (1)
C(11)	0.0099 (5)	0.0028 (1)	0.0029 (1)	−0.0007 (2)	−0.0002 (2)	−0.0000 (1)
C(12)	0.0107 (5)	0.0030 (1)	0.0031 (1)	−0.0010 (2)	−0.0001 (2)	−0.0002 (1)
C(13)	0.0140 (6)	0.0031 (1)	0.0030 (1)	−0.0016 (2)	−0.0009 (2)	0.0001 (1)
C(14)	0.0109 (5)	0.0035 (1)	0.0031 (1)	−0.0014 (2)	−0.0004 (2)	−0.0002 (1)
Li(2)	0.0161 (9)	0.0042 (2)	0.0035 (2)	−0.0017 (4)	−0.0005 (4)	0.0002 (2)
Li(1)	0.0133 (9)	0.0037 (2)	0.0034 (2)	−0.0010 (4)	−0.0002 (3)	−0.0004 (2)
A1C(1)	0.0215 (8)	0.0062 (2)	0.0092 (3)	−0.0009 (4)	−0.0038 (4)	0.0007 (2)
A1C(2)	0.0266 (9)	0.0075 (2)	0.0056 (2)	−0.0015 (4)	−0.0023 (3)	−0.0011 (2)
A1C(3)	0.0459 (14)	0.0079 (3)	0.0086 (3)	−0.0040 (5)	0.0105 (5)	−0.0019 (2)
A1C(4)	0.0309 (10)	0.0056 (2)	0.0078 (2)	−0.0017 (4)	−0.0029 (4)	0.0021 (2)
A1C(5)	0.0280 (9)	0.0087 (3)	0.0067 (2)	−0.0098 (4)	−0.0053 (4)	0.0036 (2)
A1C(6)	0.0261 (9)	0.0117 (3)	0.0048 (2)	−0.0110 (5)	−0.0030 (3)	0.0022 (2)
A1N(2)	0.0149 (5)	0.0047 (1)	0.0037 (1)	−0.0020 (2)	−0.0007 (2)	0.0004 (1)
A1N(1)	0.0174 (5)	0.0039 (1)	0.0037 (1)	−0.0010 (2)	−0.0005 (2)	0.0004 (1)
A2C(1)	0.0245 (8)	0.0079 (2)	0.0037 (2)	0.0027 (4)	−0.0004 (3)	−0.0003 (2)
A2C(2)	0.0305 (9)	0.0067 (2)	0.0047 (2)	0.0053 (4)	−0.0002 (3)	−0.0002 (2)
A2C(3)	0.0300 (9)	0.0067 (2)	0.0037 (2)	−0.0050 (4)	0.0007 (3)	0.0000 (2)
A2C(4)	0.0294 (9)	0.0042 (2)	0.0078 (2)	−0.0000 (4)	−0.0017 (4)	0.0016 (2)
A2C(5)	0.0207 (7)	0.0062 (2)	0.0042 (2)	−0.0047 (3)	−0.0007 (3)	0.0002 (1)
A2C(6)	0.0250 (8)	0.0050 (2)	0.0045 (2)	−0.0027 (3)	−0.0030 (2)	−0.0006 (1)
A2N(1)	0.0166 (5)	0.0044 (1)	0.0029 (1)	0.0006 (2)	−0.0006 (2)	−0.0003 (1)
A2N(2)	0.0177 (5)	0.0036 (1)	0.0031 (1)	−0.0011 (2)	−0.0009 (2)	0.0004 (1)

Table IV. Interatomic Distances (Å) for $[\mathrm{LiTMED}]_2\mathrm{C}_{14}\mathrm{H}_{10}$

Atoms		Atoms	
C(1)–C(2)	1.413 (5)	Li(1)–C(9)	2.345 (6)
C(1)–C(11)	1.413 (4)	Li(1)–C(10)	2.332 (6)
C(2)–C(3)	1.365 (5)	Li(1)–C(11)	2.581 (6)
C(3)–C(4)	1.409 (5)	Li(1)–C(12)	2.570 (6)
C(4)–C(12)	1.403 (4)	Li(1)–C(13)	2.454 (6)
C(5)–C(13)	1.406 (5)	Li(1)–C(14)	2.451 (6)
C(5)–C(6)	1.406 (6)	Li(2)–A2N(1)	2.115 (6)
C(6)–C(7)	1.353 (6)	Li(2)–A2N(2)	2.106 (6)
C(7)–C(8)	1.393 (5)	Li(1)–A1N(1)	2.103 (6)
C(8)–C(14)	1.408 (5)	Li(1)–A1N(2)	2.073 (6)
C(9)–C(11)	1.420 (4)	A1C(1)–A1N(2)	1.449 (5)
C(9)–C(14)	1.432 (4)	A1C(2)–A1N(2)	1.459 (5)
C(10)–C(12)	1.426 (4)	A1C(3)–A1N(1)	1.421 (5)
C(10)–C(13)	1.430 (4)	A1C(4)–A1N(1)	1.446 (5)
C(11)–C(12)	1.450 (4)	A1C(5)–A1N(1)	1.449 (5)
C(13)–C(14)	1.431 (4)	A1C(6)–A1N(2)	1.447 (4)
Li(2)–C(1)	2.378 (7)	A1C(6)–A1C(5)	1.370 (5)
Li(2)–C(2)	2.273 (7)	A2C(1)–A2N(1)	1.465 (4)
Li(2)–C(3)	2.277 (7)	A2C(2)–A2N(1)	1.452 (4)
Li(2)–C(4)	2.395 (6)	A2C(3)–A2N(2)	1.468 (4)
Li(2)–C(11)	2.667 (6)	A2C(4)–A2N(2)	1.450 (5)
Li(2)–C(12)	2.671 (5)	A2C(5)–A2N(2)	1.463 (4)
		A2C(6)–A2N(1)	1.461 (4)
		A2C(6)–A2C(5)	1.502 (5)

A suitable crystal (0.5 × 0.3 × 0.3 mm) was chosen for structural analysis and mounted so that the c^* axis was coincident with the θ axis of the diffractometer. Several ω scans gave a full peak width at half-height of 0.17° indicating that the crystal was acceptable for data collection. A survey of various reflections showed that a 2θ scan of 2.0° was necessary to obtain all the peak intensity. A full form of data (hkl) and $(\bar{h}kl)$ was measured to $2\theta_{\max} = 60°$, giving a total of 7518 reflections. Of the unique data, 2462 reflections were considered observed using the criteria $I_{\mathrm{obsd}} > 3\sigma_i(I)$ where

$$\sigma_i = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$$

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. To save on computing time, only the 2462 observed reflections were used in the refinement. The remainder of the data collection details is the same as reported previously.

Solution. The structure was solved by the symbolic addition procedure using the programs FAME and MULTAN. The 14 carbon atoms of the anthracene ring system were found on the first E map. On the subsequent Fourier, the four nitrogen atoms were found. The remaining nonhydrogen atoms were located from the next Fourier. One cycle of full-matrix least-squares refinement of the scale factor and all positional parameters using ORFLSD gave a weighted R factor

$$R_2 = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^{\,2}]^{1/2} = 0.24$$

After an additional cycle of varying the positional parameters, the thermal parameters were varied isotropically along with the positional parameters. Five cycles resulted in isotropic convergence with a weighted R factor of 0.15. The hydrogen atoms were then added at calculated positions using the program HYGEN. Each hydrogen atom was given as isotropic thermal parameter equal to that of its parent carbon atom and placed 1.0 Å from that atom. One more cycle of isotropic refinement of nonhydrogen atoms gave $R_2 = 0.11$. Further refinement after conversion to anisotropic thermal parameters led to R factors

$$R_1 = \Sigma\frac{||F_o|-|F_c||}{\Sigma|F_o|} = 0.071$$

$$R_2 = 0.073$$

The hydrogen atoms bonded to the anthracene group were refined isotropically to give $R_1 = 0.063$ and $R_2 = 0.066$ with ERF = 2.48. The standard deviations used in the weighting scheme were calculated according to the equation

$$\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2) + k(\mathrm{Int})^2]^{1/2}$$

$$\sigma(F) = F_o/2\frac{(\sigma_c)}{(\mathrm{Int})}$$

where the symbols have the meaning previously explained, with Int = integrated intensity and $k = 0.03$. A test of the weighting scheme showed no significant variation of $w(|F_o| - |F_c|)^2$ with the magnitude of the F_o or with respect to $\sin\theta/\lambda$. The maximum peak intensity on a final difference Fourier was 0.2 e/Å^3.

Table V. Interatomic Angles (deg) for [LiTMED]$_2$C$_{14}$H$_{10}$

C(11)–C(1)–C(2)	122.7 (4)	C(3)–Li(2)–C(4)	35.0 (1)
C(1)–C(2)–C(3)	118.9 (4)	C(3)–Li(2)–C(11)	69.7 (2)
C(2)–C(3)–C(4)	119.8 (4)	C(3)–Li(2)–C(12)	59.2 (2)
C(3)–C(4)–C(12)	122.7 (4)	C(1)–Li(2)–C(4)	70.4 (2)
C(13)–C(5)–C(6)	121.9 (5)	C(1)–Li(2)–C(11)	31.9 (1)
C(5)–C(6)–C(7)	119.8 (5)	C(1)–Li(2)–C(12)	57.6 (2)
C(6)–C(7)–C(8)	120.5 (5)	C(4)–Li(2)–C(11)	57.3 (2)
C(7)–C(8)–C(14)	121.6 (4)	C(4)–Li(2)–C(12)	31.5 (1)
C(14)–C(9)–C(11)	123.2 (3)	C(10)–Li(1)–C(9)	72.1 (2)
C(12)–C(10)–C(13)	123.4 (3)	C(10)–Li(1)–C(14)	61.5 (2)
C(1)–C(11)–C(12)	117.4 (3)	C(10)–Li(1)–C(13)	34.7 (1)
C(9)–C(11)–C(12)	117.6 (3)	C(10)–Li(1)–C(12)	33.4 (1)
C(4)–C(12)–C(11)	117.6 (3)	C(10)–Li(1)–C(11)	59.6 (1)
C(10)–C(12)–C(11)	116.9 (3)	C(9)–Li(1)–C(14)	34.7 (1)
C(10)–C(13)–C(14)	117.6 (3)	C(9)–Li(1)–C(13)	61.3 (2)
C(5)–C(13)–C(14)	117.7 (4)	C(9)–Li(1)–C(12)	59.7 (2)
C(9)–C(14)–C(13)	117.5 (3)	C(9)–Li(1)–C(11)	33.1 (1)
C(8)–C(14)–C(13)	118.5 (3)	C(14)–Li(1)–C(13)	33.9 (1)
C(1)–Li(2)–C(2)	35.3 (2)	C(14)–Li(1)–C(12)	70.5 (2)
C(2)–Li(2)–C(3)	34.9 (1)	C(14)–Li(1)–C(11)	59.7 (2)
C(2)–Li(2)–C(11)	59.6 (2)	C(13)–Li(1)–C(12)	60.0 (2)
C(2)–Li(2)–C(12)	69.9 (2)	C(13)–Li(1)–C(11)	70.0 (2)
C(2)–Li(2)–C(4)	61.8 (2)	C(12)–Li(1)–C(11)	32.7 (1)
C(3)–Li(2)–C(1)	61.8 (2)	C(11)–Li(1)–A1N(1)	101.0 (2)
C(2)–Li(2)–A2N(1)	109.7 (2)	C(13)–Li(1)–A1N(2)	104.0 (2)
C(12)–Li(2)–A2N(2)	96.1 (2)	A1N(1)–Li(1)–A1N(2)	85.9 (2)
		A2N(1)–Li(2)–A2N(2)	85.7 (2)
A2C(1)–A2N(1)–A2C(2)	108.8 (3)	A1C(3)–A1N(1)–A1C(4)	108.9 (4)
A2C(1)–A2N(1)–A2C(6)	109.7 (3)	A1C(3)–A1N(1)–A1C(5)	112.5 (4)
A2C(2)–A2N(1)–A2C(6)	110.9 (3)	A1C(4)–A1N(1)–A1C(5)	110.0 (3)
A2C(3)–A2N(2)–A2C(4)	109.3 (3)	A1C(1)–A1N(2)–A1C(2)	106.6 (3)
A2C(3)–A2N(2)–A2C(5)	109.9 (3)	A1C(1)–A1N(2)–A1C(6)	110.3 (3)
A2C(4)–A2N(2)–A2C(5)	111.2 (3)	A1C(2)–A1N(2)–A1C(6)	111.4 (4)
A2N(1)–A2C(5)–A2C(6)	112.3 (3)	A1N(1)–A1C(5)–A1C(6)	119.7 (3)
A2N(2)–A2C(6)–A2C(5)	112.0 (3)	A1N(2)–A1C(6)–A1C(5)	118.2 (3)

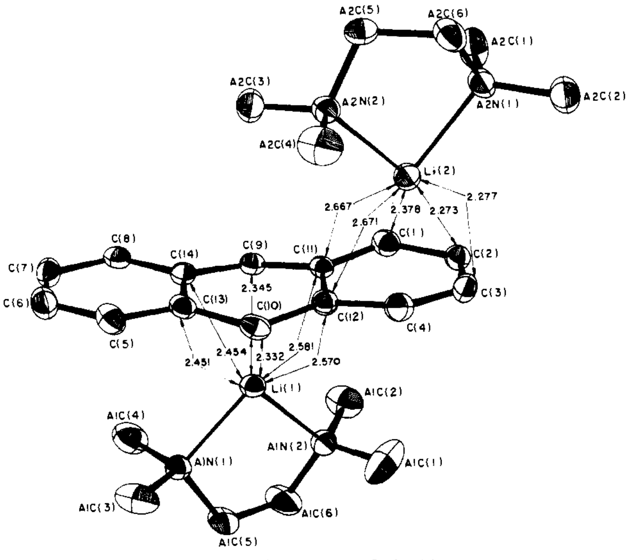


Figure 1. Molecular structure of [LiTMED]$_2$C$_{14}$H$_{10}$.

Because of limited core storage on the Sigma 5 computer, the refinement was done by refining the anthracene fragment and two TMEDA's separately. Atomic coordinates and temperature parameters are given in Tables I-III. Interatomic distances and angles are given in Tables IV and V. A listing of structure factor amplitudes is also included (supplementary material).

Results and Discussion

Lithium Atom Environment. The molecule structure of {Li[(CH$_3$)$_2$N(CH$_2$)$_2$N(CH$_3$)$_2$]}$_2$C$_{14}$H$_{10}$ consists of a C$_{14}$H$_{10}$ group coordinated to two lithium atoms, each of which is coordinated in a bidentate fashion to an *N,N,N′,N′*-tetramethylethylenediamine group (Figure 1). The coordination sphere of each lithium atom contains two tertiary amine nitrogen atoms and one unsaturaged organic group as in benzyllithium triethylenediamine,[6] fluorenyllithium bisquinuclidine,[8] triphenylmethyllithium tetramethylethylenediamine,[7] and indenyllithium tetramethylenediamine.[9] The positions of the two lithium atoms with respect to the anthracene ring are shown in Figure 2. This configuration is one of those (b) discussed in the introductory section for this compound with one lithium atom 2.453 (6) ± 0.002 Å from C(13) and C(14), 2.338 (6) ± 0.006 Å from C(9) and C(10), 2.575 (6) ± 0.006 Å from C(11) and C(12), and 2.053 (5) Å above the mean plane of the C(11)-C(14) atoms (Table VI) with an average Li-C distance of 2.44 Å. The corresponding position of the lithium atom in [TMEDLi]$_2$(naphthalenide) is 2.261 (10) ± 0.005 Å from C(2) and C(3), 2.324 (10) ± 0.003 Å from C(1) and C(4), and 2.660 (10) ± 0.005 Å from C(11) and C(12), i.e., almost identical with the second lithium position described above. The Cr atom in Cr(CO)$_3$C$_{14}$H$_{10}$[10] (Figure 3) is also displaced to the outer edge of the anthracene molecule but to a lesser extent than observed for the outer lithium atom in [TMEDLi]$_2$(anthracenide). In spite of the fact that the difference in the lithium and chromium atomic (metallic) radii is 0.28 Å, the difference between the average Cr-C and Li-C anthracene distances is only 0.193 Å.

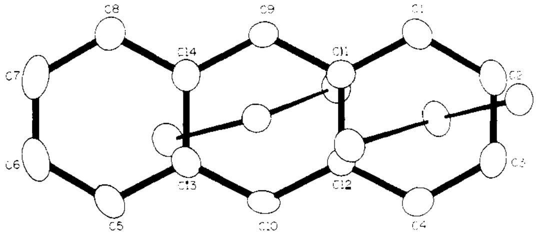
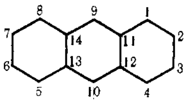


Figure 2. Orientation of the N-Li-N fragments with respect to the anthracene molecule in [LiTMED]$_2$C$_{14}$H$_{10}$.

Table VI. Best Plane Calculations for [LiTMED]$_2$(anthracene)[a]



Plane	Atoms in plane	Equation	χ^2
1	C(1), C(2), C(11)	$-0.7223x - 0.6913y - 0.0180z - 0.1147 = 0$	
2	C(11), C(12), C(2), C(3)	$-0.8013x - 0.5980y - 0.0182z - 0.3572 = 0$	0.18
3	C(9), C(11), C(14)	$-0.9267x - 0.3730y - 0.0448z - 0.6925 = 0$	
4	C(11), C(12), C(13), C(14)	$-0.8054x - 0.5900y - 0.0564z - 0.1610 = 0$	15.14
5	C(14), C(8), C(7)	$-0.7970x - 0.5923y - 0.1187z + 0.0483 = 0$	
6	C(14), C(13), C(6), C(7)	$-0.8084x - 0.5760y - 0.1212z + 0.0144 = 0$	3.48
7	C(14), C(11), C(12)	$-0.8012x - 0.5961y - 0.0520z - 0.1668 = 0$	
8	C(11), C(12), C(13)	$-0.8010x - 0.3956y - 0.0610z - 0.1151 = 0$	
9	C(1), C(2), C(3), C(4)	$-0.7981x - 0.5968y - 0.0829z + 0.1786 = 0$	0.02
10	C(1), C(4), C(11), C(12)	$0.7989x + 0.5997y - 0.0456z + 0.7147 = 0$	0.71
11	C(10), C(11), C(12), C(9)	$0.8021x + 0.5923y - 0.0759z + 0.9087 = 0$	7.51
12	C(9), C(10), C(13), C(14)	$-0.7952x - 0.5767y - 0.1872z + 0.2536 = 0$	5.99
13	C(5), C(8), C(13), C(14)	$-0.8081x - 0.5734y - 0.1349z + 0.0535 = 0$	3.46
14	C(5), C(6), C(7), C(8)	$-0.8122x - 0.5735y - 0.1071z - 0.0086 = 0$	0.65
15	C(11), C(13), Li(1), A1N(1), A1N(2)	$0.5752x - 0.7019y - 0.4201z + 4.3443 = 0$	10,031.8
16	C(11), Li(1), A1N(2)	$0.5114x - 0.7429y - 0.4319z + 4.2274 = 0$	
17	C(13), Li(1), A1N(1)	$0.6470x - 0.6604y - 0.3811z + 4.4373 = 0$	
18	C(2), C(12), Li(2), A2N(1), A2N(2)	$0.5742x - 0.7129y - 0.4026z + 5.3391 = 0$	9493.7
19	C(2), Li(2), A2N(1)	$0.6599x - 0.6353y - 0.4012z + 5.1324 = 0$	
20	C(12), Li(2), A2N(2)	$0.5109x - 0.7750y - 0.3720z + 5.2821 = 0$	

	Planes around Li1				Planes around Li2				
Atom	15	16	17	Atom	18	19	20	Dihedral angles (deg)	
C11	0.139(3)	0		C2	0.232(4)	0		4–15	88.5
C13	−0.160(3)		0	C12	−0.119(3)		0	2–18	88.5
Li1	−0.031(5)	0	0	Li2	−0.006(6)	0	0	16–17	9.6
1N1	0.146(3)		0	2N1	−0.178(4)	0		19–20	11.8
1N2	−0.138(3)	0		2N2	0.179(4)		0		

Atom	1	2	3	4	5	6
Li(1)			2.168 (5)	2.053 (5)		
Li(2)	−2.063 (6)	−1.994 (5)				
C(1)	0.000 (4)	−0.083 (4)				
C(2)	0.000 (4)	−0.001 (4)				
C(3)		0.001 (4)				
C(4)		−0.076 (4)				
C(5)						−0.023 (4)
C(6)						−0.006 (5)
C(7)					0.000 (3)	0.006 (5)
C(8)					0.000 (3)	−0.012 (4)
C(9)			0.000 (3)	0.168 (3)		
C(10)				0.166 (3)		
C(11)	0.000 (3)	0.000 (3)	0.000 (3)	−0.005 (3)		
C(12)		0.000 (3)		0.005 (3)		
C(13)				−0.006 (3)		0.002 (3)
C(14)			0.000 (3)	+0.006 (3)	0.000 (3)	−0.002 (3)
H(1)	0.135 (30)	−0.065 (30)				
H(2)		0.00 (3)				
H(3)		0.05 (3)				
H(4)		−0.15 (3)				
H(5)						−0.006 (5)
H(8)					0.008 (31)	
H(9)			−0.18 (3)	0.23 (3)		
H(10)				0.21 (3)		
A1N(1)				3.544 (3)		
A1N(2)				3.614 (3)		
A2N(1)		−3.533 (4)				
A2N(2)		−3.547 (4)				

Atom	7	8	9	10
Li(1)				
C(1)			0.000 (4)	0.001 (4)
C(2)			0.000 (4)	
C(3)			0.000 (4)	
C(4)			0.000 (4)	−0.001 (4)
C(5)				
C(6)				
C(7)				
C(8)				
C(9)				
C(10)				
C(11)	0.000 (3)	0.000 (3)		−0.001 (3)
C(12)	0.000 (3)	0.000 (3)		0.001 (3)
C(13)		0.000 (3)		
C(14)	0.000 (3)			
H(1)			0.02 (3)	
H(2)			−0.05 (3)	
H(3)			0.00 (3)	
H(4)			−0.08 (3)	
H(5)				
H(8)				
H(9)				
H(10)				

Dihedral Angle			Dihedral Angle		
between planes 1 and	2 is	7.013	between planes 10 and	11 is	1.798
3	4	14.295	11	12	−15.153
5	6	1.147	12	13	3.094
7	8	0.528	13	14	1.606
9	10	−7.370			

---

[a] Notes on mean planes. From plane 1. The hydrogen atom 1 is bent away from Li being 0.13 (3) out of plane 1, and in plane 3, hydrogen 9 is 0.18 (3) out of plane and bent away from Li. However, in plane 5, the hydrogen 8 is located in the same plane as carbon 7, 8, and 14. Plane 4. C(11), C(12), C(13), C(14) are not exactly planar, but plane 7 and 8 show twist in the boat form is only 0.53°.

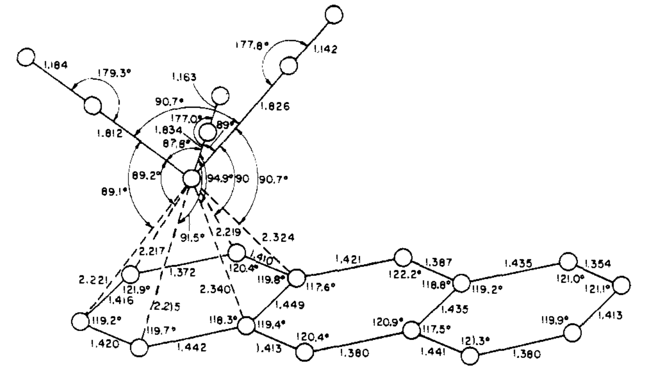


Figure 3. Molecular structure of $Cr(CO)_3C_{14}H_{10}$ taken from F. Hanic and O. S. Mills, *J. Organomet. Chem.*, **11**, 151 (1968).

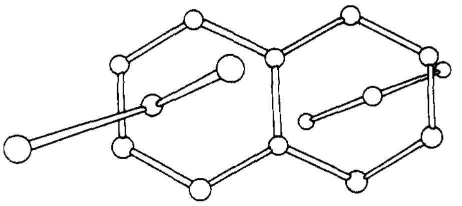


Figure 4. Orientation of the N-Li-N fragments with respect to the naphthalene molecule in $[LiTMED]_2C_{10}H_8$.

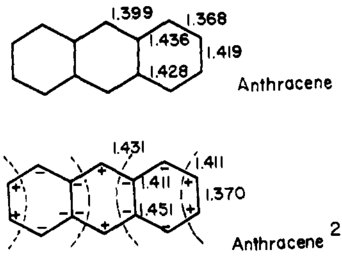


Figure 5. Comparison of averaged bond lengths of the anthracene group in anthracene and $[LiTMED]_2$(anthracenide). The symmetry of the highest unoccupied molecular orbital of anthracene is shown for the latter compound.

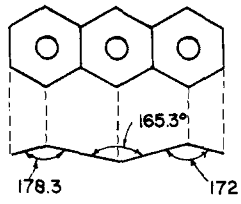


Figure 6. Nonplanarity of the anthracene fragment in $[LiTMED]_2C_{14}H_{10}$.

The average Li-C distance of the lithium atoms bonded to six-membered rings is 2.44 Å and is 0.11 Å longer than the average Li-C distance of 2.33 Å observed in indenyllithium,[9] where the lithium atom is bonded to a five-membered ring.

The orientation of the N-Li-N planes with respect to the anthracene plane (Figure 2) is almost identical, with angles of 16 ± 2° between the N-Li-N planes and a vertical plane passing through the midpoints of the C(2)-C(3), C(11)-C(12), C(13)-C(14), and C(6)-C(7) bonds. This value is also identical with that observed for the two N-Li-N planes in $[TMEDLi]_2$(naphthalenide) (Figure 4). The nitrogen atoms are also observed to be located approximately over carbon atoms in the six-membered rings. The nitrogen and the carbon atoms in the rings form an approximate plane which has a dihedral angle of 88.5° with the plane of the ring. The sum of the angles around Li(1) and Li(2) is 360.9 and 361.4°, respectively. The average Li(1)-N distance of 2.089 (6) Å is shorter than the average Li(2)-N distance of 2.110 (6) Å.

Carbanion Geometry. A comparison of the averaged bond lengths for anthracene[11] and the anthracene fragment in $[LiTMED]_2$(anthracenide) is shown in Figure 5. There is a correlation with the symmetry expected for the HOMO of anthracene, with C(1)-C(2) increasing 0.043 (6) Å, C(2)-C(3) decreasing to 0.049 (6) Å, C(1)-C(11) decreasing 0.025 (6) Å, and C(9)-C(11) increasing 0.041 (6) Å. C(11)-C(12) have small MO coefficients of the same sign which predicts a decrease in this bond length contrary to the observed increase of 0.023 (6) Å. In naphthalene and $[LiTMED]_2$(naphthalenide), there is a similar increase (0.029 (10) Å) in the C(9)-C(10) bond length. The naphthalene C(9)-C(10) interaction should be nonbonding according to the symmetry of the HOMO of naphthalene.

The magnitudes of the changes in the bond lengths in anthracene and $[LiTMED]_2$(anthracenide) are somewhat less than in naphthalene and $[LiTMED]_2$(naphthalene). This is to be expected since the HOMO of anthracene is delocalized over 24 nuclear centers rather than the 18 in naphthalene. Assuming equal delocalization over each center, the bonding and antibonding contributions to a given bond in anthracene should be ~75% of those in naphthalene. The 2-3 bond length change going from naphthalene to $[LiTMED]_2$(naphthalenide) is 0.072 (10) Å, while the corresponding change in anthracene is 0.049 (6) Å or 60% of that in naphthalene. The factor for the 1,2 bond is 62%.

The distortion of the anthracene molecule in the outer six-membered rings from planarity also is less than that for naphthalene as illustrated by Table VI and Figure 6. The value of 172.7° is approximately 8° greater than the value of 164° in $[LiTMED]_2$(naphthalenide). An important question is how much of the deviation from nonplanarity is due to the proximity of the lithium atom. It would appear that most of it is, since a dihedral angle of 178.3° is observed for the six-membered ring of the anthracene molecule to which a lithium atom is not coordinated. It is undoubtedly true, however, that the formally 4n π systems, $(anthracene)^{2-}$ and $(naphthalene)^{2-}$ are easily distorted from planarity relative to the parent hydrocarbons. C(9) and C(10) are predicted to carry the largest charge in anthracene,[2] and it is at this point that the greatest deviation from planarity takes place. In fact, the value of 165.3° is quite comparable to the 164° angle in $[LiTMED]_2$(naphthalenide).

It is obvious from a comparison of Figures 3 and 5 that, whereas the bond lengths in the anthracene fragment are perturbed very little in $Cr(CO)_3$(anthracene), this is not the case in $[LiTMED]_2$(anthracenide). This suggests a greater net transfer of charge in the lithium compound from the metal to the atomatic group.

As noted in the introductory section, we have previously demonstrated that the hyperfine coupling constants of radical π carbanions are very sensitive to angular distortions of the carbanion from planarity. A significantly improved fit of the magnitudes of the observed and calculated hyperfine coupling constants for the naphthalene radical anion (contact ion pair) is obtained when the nonplanar geometry found for the solid state structure of the dianion is used as the framework for open shell INDO[5] monoanion calculations. In the naphthalene radical contact ion pair, there are two equivalent positions for the lithium atom. This is not the case for the anthracene contact ion pair. A number of

Table VII. Calculated and Observed Hyperfine Coupling Constants for the Anthracene Radical Anion

	Obsd[a]	Planar[b]	Crystal[c] coordinates	Obsd[d]	Li over[e] center ring	Li over[f] outer ring
C(1)	3.57	4.68	5.47			
	Δ_{obsd}	−1.11	−1.90			
C(2)	−0.25	0.06	−0.16			
	Δ_{obsd}	−0.31	−0.09			
C(9)	8.76	12.29	16.11			
	Δ_{obsd}	−3.53	−7.35			
C(11)	−4.59	−3.59	−3.92			
	Δ_{obsd}	−1.00	−0.67			
H(1)	−2.74 (2.395)	−2.73	−2.60	(−)2.74 (2.395)	−1.52	−2.58
	Δ_{obsd}	−0.01	−0.14	Δ_{obsd}	−1.22	−0.16
H(2)	−1.51 (1.291)	−0.58	−0.46	(−)1.57 (1.291)	−0.62	−0.18
	Δ_{obsd}	−0.93	−1.05	Δ_{obsd}	−0.95	−1.39
H(9)	−5.34 (5.800)	−6.80	−6.18	(−)5.56 (5.800)	−5.45	−5.12
	Δ_{obsd}	+1.46	+0.84	Δ_{obsd}	−0.11	−0.42

[a] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, 40, 3307 (1964). These values are for a solvent separated dimethoxyethane organolithium species. Values in parentheses are from A. H. Reddock, *ibid.*, 43, 225 (1965) and are for a diethyoxyethane potassium contact ion pair. [b] Anthracene coordinates, ref 10. [c] Geometry is that of an isolated naphthalene fragment with the bond distances and angles taken from the present study. [d] A. Carrington, F. Drovnick, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959). These values are for a tetrahydrofuran potassium species (contact ion pair). [e] Averaged coordinates of two outer six-membered rings. [f] As in *c* above with lithium atom included.

open shell INDO calculations were made for the anthracene radical anion assuming various molecular geometries. The results for a planar configuration and the nonplanar geometry observed here are tabulated in Table VII. The magnitudes of the hyperfine coupling constants for the planar and crystal coordinate geometries fit nearly equally poorly (or well) by the goodness of fit criteria $R = \Sigma\Delta/\Sigma_{obsd}$ with $R_{planar} = 0.28$ and $R_{crystal} = 0.23$ where Δ = difference between the observed and calculated hyperfine coupling constants and Σ_{obsd} = sum of observed hyperfine coupling constants. The crystal geometry calculation does predict that the sign of the C(2) hyperfine coupling constant should be negative which agrees with experimental results. Going from a solvent separated to a contact ion pair shifts the hyperfine coupling constants slightly. The coupling constants of H(2) and H(9) give a better fit for the lithium atom over the center ring, while that for H(1) is better for a lithium atom over an outer ring of the anthracene molecule. Both species are probably simultaneously present in solution and the observed data may represent a weighted average of the two geometries. Since no ESR data for a lithium contact ion pair system are available, a more quantitative comparison is not possible. It has been noted, however, that radical contact ion pairs formed with anthracene and lithium give anomalous hyperfine coupling constants.[12]

Acknowledgment. The support of The National Science Foundation under Grants NSF DMR 7203026 and NSF MPS 7423000 is greatly appreciated.

Supplementary Material Available. A stereographic projection of unit cell constants in bis[(tetramethylethylenediamine)lithium(I)] anthracenide and listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2079.

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