Journal of Organometallic Chemistry, 134 (1977) 139—149

1,2-HYDROGEN ABSTRACTION: THE CHARACTERIZATION OF $[Li(CH_3)_2N(CH_2)_2N(CH_3)_2]_2$ $[C_{12}H_8]$. A DILITHIUM COMPLEX OBTAINED BY THE 1,2 DEPROTONATION OF ACENAPHTHYLENE

WENDELL E. RHINE, JIMMY H. DAVIS and GALEN STUCKY
Department of Chemistry, School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

(Received December 27th, 1976)

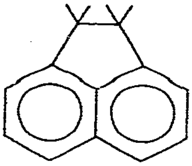
Summary

The reaction of n-butyllithium chelated to *N,N,N',N'*-tetramethylethylenediamine (TMEDA) with acenaphthene results in 1,2-hydrogen abstraction to give the dilithio complex of acenaphthylene, $[Li(CH_3)_2N(CH_2)_2N(CH_3)_2]_2[C_{12}H_8]$. This compound was isolated as a crystalline product and characterized by single crystal X-ray crystallography. $[Li(CH_3)_2N(CH_2)_2N(CH_3)_2]_2[C_{12}H_8]$ crystallizes with a unit cell of a = 23.164(10), b = 25.609(10) and c = 8.495(6) Å in the orthorhombice space group *Fdd*2. The calculated density is 1.04 g cm^{-3} for 8 molecules per unit cell. The observed density is 1.03(4) g cm^{-3}. 1412 unique reflections were measured on a full circle X-ray diffractometer. The light atom, acentric structure was solved by the symbolic addition technique and refined by full matrix least squares to R_1 = 0.058 and R_2 = 0.056.

The acenaphthylene fragment is nearly planar. The effect of charge transfer is evidenced in the short C(3)—C(4) bond distance of 1.30(3) Å and the lengthening of the C(1)—C(2) bond length from the localized olefinic bond distance of 1.34 to 1.42(2) Å. The two LiTMEDA fragments are coordinated to both sides of the five membered carbon atom ring of the acenaphthylene group.

Introduction

A number of examples of proton abstraction by *N*-chelated organolithium reagents to give dianions from 1,4-dihydro aromatic hydrocarbons [1—6] are now known. The power of this method is evident by the fact that 1,2-proton abstraction is possible for 1,2-dihydro olefins such as 1,2-diphenylethane and bifluorenyl [6]. In this paper, we describe the results of 1,2-proton abstraction from acenaphthene (I) to give the dilithio complex of acenaphthylene, $[Li(CH_3)_2N(CH_2)_2N(CH_3)_2]_2[C_{12}H_8]$.



(I)

A point of interest in this study is that while acenaphthylene is a $4n\pi$-electron system and is not aromatic according to the Hückel $(4n + 2)\pi$-electron rule, the dianion is formally a $(4n + 2)\pi$-electron system and is aromatic, so that the reduced form of acenaphthylene should be relatively stable. In contrast, the reduced forms of anthracene and naphthalene, which we have studied previously, are formally $4n\pi$-electron systems while the neutral molecules are $(4n + 2)\pi$-electron systems and therefore aromatic. This report describes the first stereochemical investigation of a main group metal coordinated $(4n + 2)$ to carbocyclic π-anion which has a $4n\pi$ precursor with the same nuclear framework.

Experimental

A 0.013 mol (2.0 g) sample of acenaphthene was added to a 300 ml flask containing 200 ml of dry hexane and 0.026 mol (3.0 g) of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) under a nitrogen atmosphere. A 20 ml (0.026 mol) sample of n-butyllithium in hexane was added to the flask via syringe. The color changed to dark-blue immediately. The reaction mixture was allowed to stand overnight. The dark blue-black needle crystals which had formed were transferred to a drybox and filtered. Recrystallization from benzene gave crystals suitable for X-ray analysis.

Crystals for single-crystal X-ray analysis were sealed in thin-walled glass capillaries in a helium atmosphere because of the sensitivity of the acenaphthylene dianion to oxygen and water. Precession and Weissenberg photographs showed that the crystals belong to the space group *Fdd*2. The lattice parameters (T 23°C, λ 0.71069 Å) determined from the least-squares refinement of 12 centered reflections on a Picker full circle diffractometer are a 23.164(10), b 25.609(10), c 8.495(6) Å. The calculated density for 8 molecules per unit cell is 1.04 g cm^{-3}. A density of 1.03(4) g cm^{-3} was measured by the flotation method in a mixture of benzene and chlorobenzene [2].

Intensity data were measured using Mo-K_α radiation on an automated Picker four-circle diffractometer equipped with a highly oriented graphite single-crystal monochromator. The crystal, a parallel piped of 0.5 × 0.4 × 0.3 mm was oriented for data collection so that the c^* axis was approximately coincident with the ϕ axis of the diffractometer. Several ω scans showed the typical full peak width at half-height to be approximately 0.16° indicating that the mosaicity was acceptably low for data collection. A survey of various peaks showed that a 2θ scan of 2.0° was sufficient to obtain all the peak intensity. Only reflections $h + k = 2n$ and $k + l = 2n$ were collected using a reject sub-routine for face-centered crystals. Data were collected to $2\theta_{max} = 53°$, giving a total of 1412 unique reflections.

Of the unique data, 558 reflections were considered observed using the criteria

$I_o > 3\sigma_c$ (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. All the data were used in the refinement. The remainder of the data collection details are the same as reported previously [3,5,6].

Solution and refinement of the structure

The measured density suggested 8 molecules per unit cell so that the molecule must be located on a crystallographic twofold axis. This means that only 16 non-hydrogen atoms needed to be located. The structure was solved by the symbolic addition procedure using the programs FAME and MULTAN. The acenaphthylene group was located on the twofold axis as expected, but the TMEDA was more difficult to locate correctly. When the correct choice of coordinates was chosen, the value of R_1 was 0.25, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$. After two additional cycles of varying all parameters, the hydrogen atoms were added at their theoretical positions based on known atom positions and hybridizations using HYGEN. Three cycles resulted in isotropic convergence with a weighted R_2 of 0.18: $R_2 = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2} = 0.18$.

Standard deviations for the structure factors were calculated from counting statistics as described previously. Further refinement of positional and thermal parameters after conversion from isotropic to anisotropic thermal parameters led to R factors: $R_1 = 0.063$ and $R_2 = 0.063$. The estimated standard deviation of an observation of unit weight was 1.37. There were no large positive peaks (greater than 0.3 $Å^{-3}$) on the last difference Fourier, but there were some very large negative peaks, e.g., between C(1) and C(2).

Since the thermal parameters of C(2) and C(3) were very large and several bond distances unusually short, the Fourier at isotropic convergence was examined and evidence of disorder was found (Fig. 1). The coordinates of the acenaphthylene moiety in pentacarbonyldiiron-acenaphthylene [7] were used as a starting point for the disordered refinement of the acenaphthylene ion as a rigid group and subsequent refinement gave $R_2 = 0.125$. The rigid group restriction was removed and each atom of the two disordered groups varied for two cycles using the program ORFXLS-3 and the option of moving the atom 0.2 of the calculated change. The acenaphthylene carbon atom positions then were reaveraged to give C_{2v} symmetry. A new rigid group coordinate system was calculated and one cycle of rigid group refinement gave $R_2 = 0.106$.

Repeating this procedure of refinement lowered the R_2 factor to 0.074. Further refinement of positional parameters and conversion to anisotropic thermal parameters led to final R factors *: $R_2 = 0.058$ (1163 reflections) and $R_1 = 0.056$ (558 reflections).

Reflections where F_o was less than 2σ were rejected by subroutine LOGIC if $F_o > F_{cal}$ and $F_o - F_{cal} > 0.5\ \sigma$. The estimated standard deviation of an observa-

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* The table of structure factors has been deposited as a NAPS Document. Please contact ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

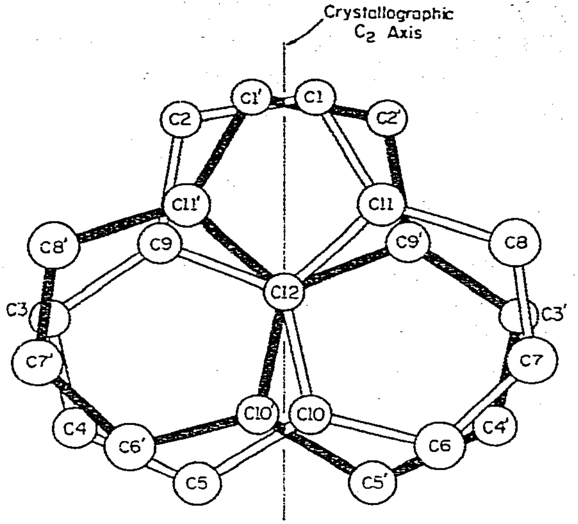


Fig. 1. Disorder found for the $C_{12}H_8$ group in the structure of $[Li(CH_3)_2N(CH_2)_2N(CH_3)_2]_2[C_{12}H_8]$.

tion of unit weight was 1.31. There were no peaks higher than 0.12 e Å^{-3} on the final difference Fourier map.

Final positional and thermal parameters are given in Tables 1 and 2. Bond distances and angles are reported in Tables 3 and 4.

TABLE 1

POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS FOR $C_{12}H_8[LiN_2C_6H_{16}]_2$ (Disordered model)

	x	*y*	*z*
C(1)	0.2362(6)	0.2523(13)	0.7352(17)
C(2)	0.2961(5)	0.2447(9)	0.7069(14)
C(3)	0.3557(6)	0.2448(6)	0.4379(15)
C(4)	0.3447(6)	0.2459(5)	0.2876(15)
C(5)	0.2895(6)	0.2486(4)	0.2105(15)
C(6)	0.1803(8)	0.2561(6)	0.2613(18)
C(7)	0.1387(6)	0.2558(7)	0.3767(19)
C(8)	0.1458(6)	0.2533(4)	0.5359(19)
C(9)	0.3060(6)	0.2471(5)	0.5380(15)
C(10)	0.2384(6)	0.2522(5)	0.3048(12)
C(11)	0.2060(6)	0.2526(6)	0.5896(16)
C(12)	0.25	0.25	0.4706
AC(1)	0.1957(3)	0.1184(2)	0.3847(7)
AC(2)	0.2966(3)	0.1076(2)	0.3891(8)
AC(3)	0.2749(2)	0.1116(2)	0.9107(9)
AC(4)	0.1772(3)	0.1315(2)	0.9134(8)
AC(5)	0.2408(2)	0.0648(2)	0.5801(7)
AC(6)	0.2101(3)	0.0716(2)	0.7233(8)
N(1)	0.2452(2)	0.1112(1)	0.4837(8)
N(2)	0.2253(2)	0.1181(1)	0.8125(6)
Li	0.2435(3)	0.1736(2)	0.6371(9)

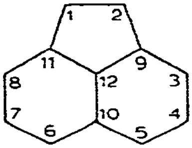
TABLE 2

ANISOTROPIC PARAMETERS FOR THE NON-HYDROGEN ATOMS FOR $C_{12}H_8[LiN_2C_6H_{16}]_2$ (Disordered model)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0027(9)	0.0014(1)	0.0130(12)	0.0014(9)	0.0011(7)	0.0014(7)
C(2)	0.0020(4)	0.0011(1)	0.0147(19)	0.0003(3)	−0.0030(6)	0.0008(6)
C(3)	0.0009(2)	0.0015(2)	0.0436(46)	0.0002(2)	0.0006(9)	0.0017(10)
C(4)	0.0038(5)	0.0011(3)	0.0468(57)	0.0005(3)	0.0040(14)	0.0002(13)
C(5)	0.0089(12)	0.0010(3)	0.0091(21)	0.0004(5)	0.0007(11)	−0.0000(8)
C(6)	0.0048(6)	0.0028(5)	0.0272(4)	−0.0006(4)	−0.0098(18)	−0.0000(13)
C(7)	0.0051(9)	0.0019(6)	0.0713(99)	−0.0009(6)	−0.0059(26)	0.0033(18)
C(8)	0.0033(7)	0.0011(3)	0.0733(91)	0.0001(4)	0.0035(19)	0.0009(13)
C(9)	0.0031(5)	0.0010(2)	0.0166(25)	−0.0000(3)	−0.0020(10)	0.0011(7)
C(10)	0.0057(8)	0.0008(2)	0.0080(17)	−0.0003(3)	0.0025(13)	0.0014(12)
C(11)	0.0013(4)	0.0009(3)	0.0240(24)	−0.0002(4)	0.0024(10)	−0.0001(9)
C(12)	0.0021(2)	0.0009(1)	0.0129(15)	0.0003(2)	—	—
AC(1)	0.0041(1)	0.0022(1)	0.0304(11)	−0.0004(1)	−0.0037(4)	−0.0006(4)
AC(2)	0.0049(2)	0.0023(1)	0.293(11)	−0.0000(1)	0.0014(5)	−0.0010(3)
AC(3)	0.0054(2)	0.0035(2)	0.0314(14)	0.0001(1)	−0.0005(5)	0.0019(4)
AC(4)	0.0050(2)	0.0033(1)	0.0257(12)	−0.0001(1)	0.0036(9)	0.0008(3)
AC(5)	0.0060(2)	0.0014(1)	0.0190(8)	−0.0004(1)	0.0013(4)	0.0005(2)
AC(6)	0.0079(2)	0.0017(1)	0.0225(10)	−0.0008(1)	0.0042(5)	0.0013(3)
N(1)	0.0030(1)	0.0014(1)	0.0148(5)	−0.0001(1)	0.0006(3)	0.0006(2)
N(2)	0.0038(1)	0.0014(1)	0.0154(6)	−0.0003(1)	0.0005(3)	0.0005(2)
Li	0.0041(2)	0.0012(1)	0.0137(4)	−0.0004(1)	−0.0005(5)	0.0014(3)

TABLE 3

INTERATOMIC DISTANCES (Å) FOR THE NON-HYDROGEN ATOMS IN $C_{12}H_8[LiN_2C_6H_{16}]_2$ (Disordered model)



Atoms	Distance	Atoms	Distance
C(1)—C(2)	1.42(2)	N(1)—Li	2.061(7)
C(1)—C(11)	1.42(2)	N(2)—Li	2.102(7)
C(2)—C(9)	1.45(1)	Li—C(1)	2.18(3)
C(3)—C(4)	1.30(3)	Li—C(2)	2.27(2)
C(3)—C(9)	1.43(2)	Li—C(9)	2.52(1)
C(4)—C(5)	1.43(2)	Li—C(12)	2.42(1)
C(5)—C(10)	1.44(2)	Li—C(11)	2.24(2)
C(6)—C(7)	1.37(2)		
C(7)—C(8)	1.36(3)	Li—C(1)′	2.13(2)
C(8)—C(11)	1.46(2)	Li—C(2)′	2.36(2)
C(9)—C(12)	1.42(2)	Li—C(9)′	2.48(1)
C(10)—C(12)	1.43(2)	Li—C(11)′	2.26(1)
C(11)—C(12)	1.44(2)		
AC(1)—N(1)	1.434(6)		
AC(2)—N(1)	1.440(6)		
AC(3)—N(2)	1.430(6)		
AC(4)—N(2)	1.447(6)		
AC(5)—N(1)	1.448(5)		
AC(6)—N(2)	1.455(6)		
AC(5)—AC(6)	1.420(7)		

TABLE 4

BOND ANGLES (deg) FOR THE NON-HYDROGEN ATOMS IN $C_{12}H_8[LiN_2C_6H_{16}]_2$ (Disordered model)

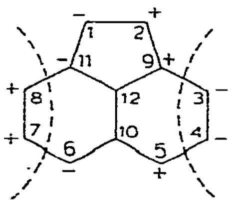
Atoms	Angle	Atoms	Angle
C(11)—C(1)—C(2)	109(1)	AC(1)—N(1)—AC(2)	110.0(4)
C(1)—C(2)—C(9)	108(2)	AC(1)—N(1)—AC(5)	112.3(4)
C(2) C(9)—C(12)	105(1)	AC(2)—N(1)—AC(5)	108.6(4)
C(9)—C(12)—C(11)	111(1)	AC(3)—N(2)—AC(4)	107.6(4)
C(1)—C(11)—C(12)	105(1)	AC(3)—N(2)—AC(6)	113.8(4)
C(9)—C(3)—C(4)	115(1)	AC(4)—N(2)—AC(6)	108.4(4)
C(3)—C(4)—C(5)	128(1)	AC(6)—AC(5)—N(1)	114.7(4)
C(4)—C(5)—C(10)	119(1)	AC(5)—AC(6)—N(2)	115.2(4)
C(7)—C(6)—C(10)	119(1)	N(1)—Li—N(2)	85.9(3)
C(8)—C(7)—C(6)	129(1)		
C(11)—C(8)—C(7)	115(1)		
C(8)—C(11)—C(12)	117(1)		
C(10)—C(12)—C(9)	125(1)		
C(10)—C(12)—C(12)	124(1)		
C(5)—C(10)—C(12)	113(1)		
C(6)—C(10)—C(12)	116(1)		
C(12)—C(9)—C(3)	120(1)		

Discussion

The observed molecular geometry is shown in Fig. 2. This is the first example of a dilithio π-organometallic complex in which the lihtium atoms are located on opposite sides of the same delocalized ring. We note, however, that in the dilithio complexes of *trans*-stilbene and bifluorenylidene [6], the lithium atoms are directly opposite each other on either side of the olefinic bond. As in other main group metal unsaturated organometallic complexes, there are significant changes observed upon reduction, in the structural properties of the unsaturated group. The discussion section is accordingly divided into two sections, first, a discussion of the unsaturated group bonding and geometry, and then a discussion of the role of the metal atom in the complex.

Bonding and structural features of the acenaphthylene group

The geometry of the $C_{12}H_8$ group is shown in Fig. 3. The anion is nearly planar, as indicated in Table 5. The symmetry of the highest occupied molecular orbital (HOMO) of the isolated carbanion (see II) is apparently preserved in the metal



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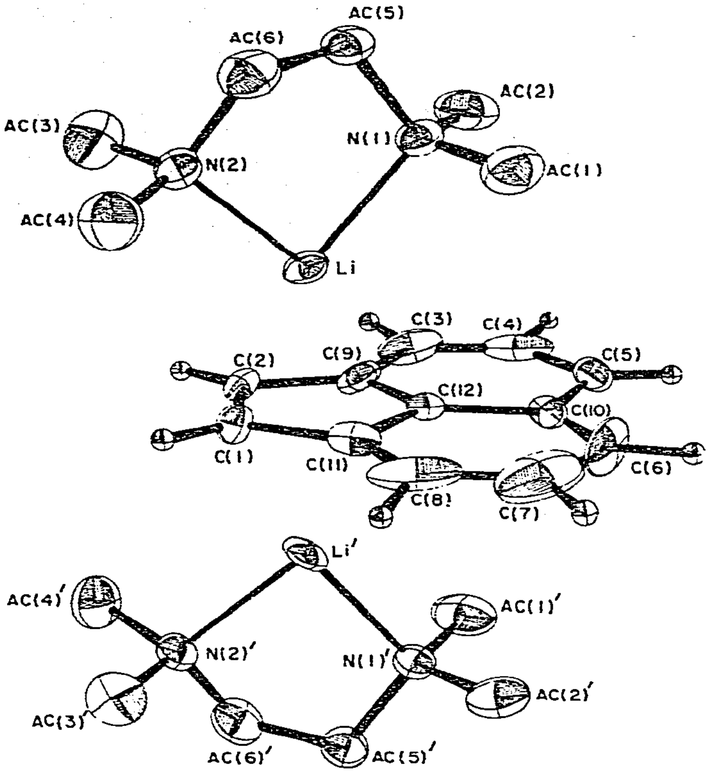

Fig. 2. Observed molecular geometry of $[\mathrm{LiTMEDA}]_2[C_{12}H_8]$.

complex. The decrease in the C(3)—C(4) bond distance from the expected aromatic distance of 1.42 Å (cf. naphthalene) to 1.30(3) Å and the increase in the C(1)—C(2) bond length from the localized olefinic bond distance of 1.34 Å to 1.42(2) Å are both consistent with this point of view. Similar changes are found for pentacarbonyldiiron-acenaphthylene [7] (Fig. 3). The corresponding distances in C(1)—C(2) and C(3)—C(4) in pentacarbonyldiiron-acenaphthylene are also consistent with some charge transfer into the $C_{12}H_8$ group. The lengthening of the C(3)—C(4) bond is very similar to that observed for the analogous C(2)—C(3) bond in the dilithio complexes of anthracene and naphthalene.

Metal atom coordination sphere

The orientation of the N—Li—N groups with respect to one of the disordered $C_{12}H_8$ fragments is shown in Fig. 3. There was no evidence of orientational disorder of the N—Li—N group. According to an INDO calculation, the N—Li—N groups are both oriented so that a lithium atom *p* orbital can overlap with the p_z orbitals of C(2′)—C(11′) and C(2)—C(11) parallel to the ring plane. Overlap of this type is consonant with the symmetry, magnitude, and the signs of the coefficients for the HOMO of the acenaphthylene group. As observed with indenyl TMEDALi, two carbon atoms in the acenaphthylene ring system and two nitrogen atoms (C(1)—C(12)—N(1)—N(2)) form a plane with the lithium atom pulled

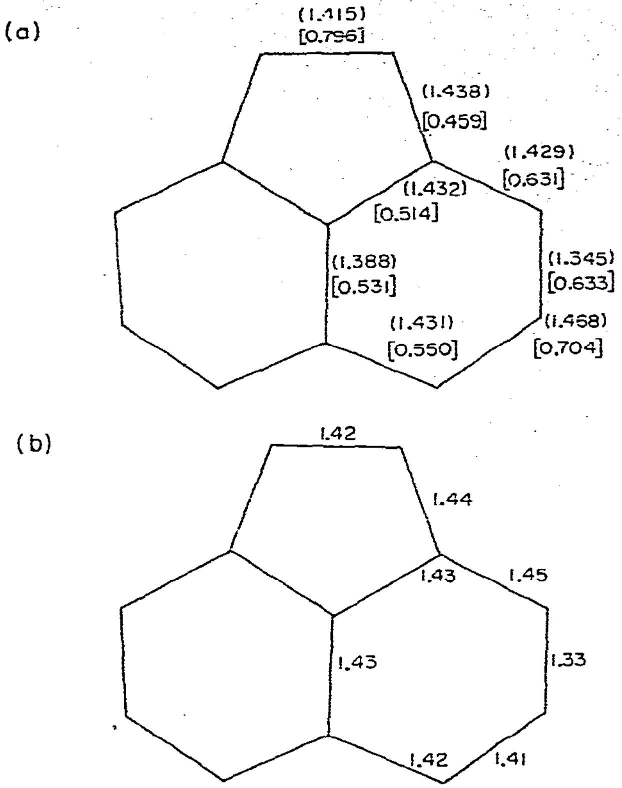

Fig. 3. (a) Bond lengths for the $C_{12}H_8$ group in $[Fe_2(CO)_5]_2C_{12}H_8$ are given in parentheses. Hückel π-bond orders for $C_{12}H_8$ (12π system) are given in brackets. (b) Bond lengths for the $C_{12}H_8$ fragment of $[Li(TMEDA)]_2C_{12}H_8$.

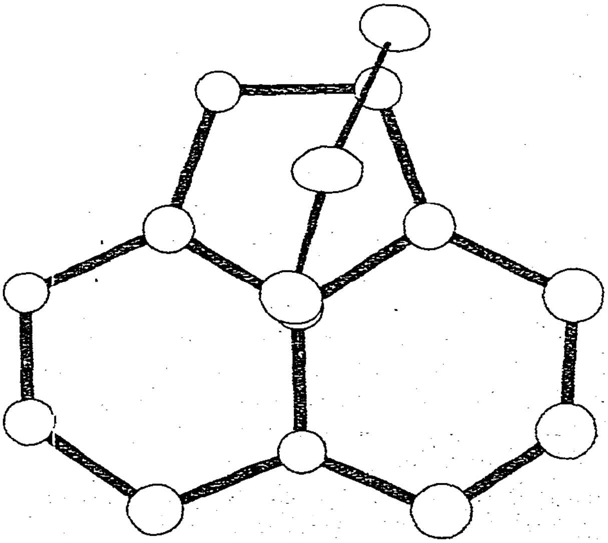

Fig. 4. Orientation of the N—Li—N groups with respect to one of the two disordered $C_{12}H_8$ groups in $[TMEDALi]_2C_{12}H_8$.

TABLE 5

WEIGHTED LEAST-SQUARE EQUATIONS THROUGH GROUPS OF ATOMS AND DEVIATIONS OF THE ATOMS FROM THESE PLANES

Atoms in plane		x^2
C(1), C(2), C(3), C(4) C(5), C(6), C(7), C(8) C(9), C(10), C(11), C(12)	$-0.0584\,x - 0.9982\,y - 0.124\,z + 6.7837 = 0$	19.2
C(1), C(12), N(1), N(2)	$-0.9875\,x + 0.0351\,y - 0.1537\,z + 6.1171 = 0$	2.5

	Deviations	
	Plane 1	Plane 2
C(1)	−0.01(2)	−0.01(1)
C(2)	0.01(2)	−1.37(1)
C(3)	−0.02(2)	
C(4)	0.01(2)	
C(5)	0.04(2)	
C(6)	−0.03(2)	
C(7)	−0.02(3)	
C(8)	0.04(2)	
C(9)	−0.02(2)	
C(10)	−0.02(2)	
C(11)	−0.02(2)	
C(12)	0.01(2)	0.01(1)
Li	1.95(2)	−0.14(1)
N(1)	3.56(2)	−0.01(1)
N(2)	3.37(2)	0.01(1)

out of the plane towards C(2). This plane makes an angle of approximately 15° with the nodal surface.

A molecular orbital calculation has been made [8] in which the lithium atom position was adjusted with respect to the acenaphthylene group to give the best fit to the ESR hyperfine coupling constants for the monolithium acenaphthylene complex. The electrostatic potential obtained for the acenaphthylene anion was found to have a minimum over the five-membered ring which is considerably steeper and deeper than that for the anthracene anion. The lithium—ring distance used in the calculations was 3.0 Å which is nearly 1 Å greater than the value found here. The lithium atom, at this distance (3.0 Å) from the ring, was predicted to be 0.57 Å from C(12). Using the atomic charge distribution obtained from a CNDO calculation for the acenaphthylene dianion, an electrostatic potential calculation predicts a minimum at 0.2 Å from C(12) for a lithium ring distance of 3.0 Å and 0.75 Å from C(12) for a lithium—ring distance of 2.0 Å. Both minimums are on the nodal plane which bisects the dianion. The observed value is 1.4 Å from C(12) with the two lithium atoms displaced off the nodal surface towards C(1) and C(2), respectively. Although the accuracy of these distances is limited because of the disorder of the organic group in the structure, it is evident that, as noted previously, the simple electrostatic model does not accurately predict the solid state structures of these complexes.

The relatively large difference between the ring—metal distance which we observe and that estimated in reference 4 suggests that it would be useful to have an empirical method of estimating the distance of metal atoms from unsaturated groups. We have recently suggested [13] a simple model based on atomic radii to do this, but considerable improvement can be obtained by taking into account changes in coordination number and/or changes in the number of valence electrons. Two methods suggested by Pauling work quite well in this respect [9]. Baker et al. [10] have discussed the application of the relation $R_i(2)/R_i(1) = CN_i(2)/CN_i(1)$, where R_i and CN_i are the bond length and coordination member of the *i*th (1st or 2nd) complex. An alternative method, also due to Pauling, is discussed below.

Cyclopentadienyllithium serves as an example of a simplified acenaphthylenyl or indenyl system. The lithium atom has one valence electron and the normal state of the molecule, as a first approximation, is that in which the lithium atom forms one bond which exhibits resonance among the five carbon atoms. The lithium carbon atom bond number (n') would then be 0.20. Substitution of the lithium atom covalent radius of 1.23 [9] in the following equation [10]: $D(\text{Li—C}) = \{R(\text{Li}) + R(\text{C}) - 0.09\ |X(\text{Li}) - X(\text{C})|\} - 0.6 \log n'$, leads with the correction for partial ionic character, to the value of 2.33 Å for the lithium—π-carbon atom distance. The electronegativity of the carbon atom was taken as the value derived from valence state ionization potentials for an electron in a carbon atom 2*p* orbital which is 1.8 and the electronegativity of lithium was taken as 0.8 [11]. The observed average lithium—carbon distance in acenapthylenyldilithium and indenyllithium is 2.33 Å.

Similar arguments for fluorenylpotassium would lead to the approximation that the potassium—carbon atom bond is among ten possible carbon atoms leading to an average bond number of 1.10 for the potassium—carbon atom bond. The potassium atom radius of 2.03 leads to the calculated and observed value of 3.33 Å. Considering only the five closest carbon atoms would give a bond number of 0.20 and a calculated distance of 3.13 Å. The average distance to the five closest carbon atoms is 3.13 Å.

The above also applies to eight-membered rings, but in the cyclooctatetraenedianion there are two valence electrons to average between the eight carbon atoms giving an average metal carbon bond number of 0.25. For example, $[\text{COTCeCl}]_2$ has an average Ce—C distance of 2.71 Å [12]. Using a Ce radius of 1.65 Å and correcting for electronegativity differences gives a calculated bond distance of 2.72 Å.

As we have stated in the past [4], our intent is not to attempt to prove that there is a large or small amount of covalent bonding in the alkali and alkaline earth carbocyclic compounds, but to arrive at the simplest model which will be useful in predicting structural and spectroscopic properties. Either of the above approaches appear to be useful as starting points in predicting metal—carbon (carbocyclic) distances. For predicting the location of the metal atom with respect to the horizontal coordinates of the carbocyclic place, a simple electrostatic model has worked quite well for potassium and sodium derivatives but not for organolithium compounds, B_2LiR (B = monodentate base, R = delocalized carbanion. For anions such as cyclooctatetraene (2—) and cyclopentadiene (—), the electrostatic minima and consideration of the symmetry properties of the HOMO predict exactly the same structure, namely with the lithium atom located directly over the centroid of the R^{n-} groups. In the benzyl, fluorenyl and, to a lesser extent, acenaphthalenyl system, this is not the case and directed orbital considerations more closely predict the positioning of the lithium atom and the orientation of the B_2Li plane.

Acknowledgment

The authors thank the National Science Foundation for support under Grants NSF-DMR-76-01058 and MPS-14-33000.

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