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π GROUPS IN ION PAIR BONDING: THE STRUCTURAL EFFECTS OF REDUCTION ON THE OLEFINIC BOND AS OBSERVED IN THE MOLECULAR STRUCTURE OF $\Delta^{9,9'}$-BIFLUORENYL BIS(LITHIUM TETRAMETHYLETHYLENEDIAMINE)

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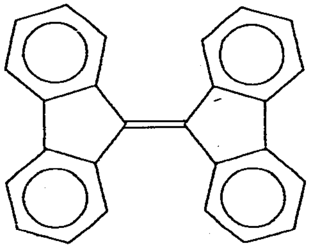
Summary

The reaction of 9,9'-bifluorene with n-butyllithium in the presence of tetramethylethylenediamine (TMEDA) results in the formation of $\Delta^{9,9'}$-bifluorenyl bis(lithium tetramethylethylenediamine). In the molecular structure of this material, which formally can be considered to be the dianion of the olefin $\Delta^{9,9'}$-bifluorene, two TMEDALi groups are closely associated with the 9,9' bond. The fluorenyl groups are twisted relative to each other by an angle of 48.0(5)°, as compared to 42° in the parent olefin. The 9,9' bond length is increased from 1.39(2) Å in $\Delta^{9,9'}$-bifluorene to 1.487(5) Å in the dianion.

Single crystal X-ray diffraction techniques were used and resulted in a final discrepancy factor of $R_w = 0.064$ for 2426 observations. The crystal system is monoclinic ($C2/c$) with $a = 10.814(3)$, $b = 16.717(6)$ and $c = 19.766(6)$ Å, $\beta = 102.55(2)°$; $\rho_{obs} = 1.10(3)$ g cm^{-3}; $\rho_{calc} = 1.094$ g cm^{-3} for four molecules per unit cell.

Introduction

Results from several investigations [1-3] of the properties of $\Delta^{9,9'}$-bifluorene have been interpreted in terms of the compound possessing some diradical character due to a twisting about the C(9)—C(9)' bond of the two fluorenyl rings.



Δ 9.9' bifluorene

The crystal structures of $\Delta^{9,9'}$-bifluorene [4] and a 1,1′-disubstituted $\Delta^{9,9'}$-bifluorene [5] have confirmed the postulated twisted geometry with an unusually long olefinic C(9)—C(9)′ bond length of 1.39(2) Å found in $\Delta^{9,9'}$-bifluorene. The formation of the dianion of the olefin can be expected to have pronounced effects on the structural properties of the organic group. Preliminary data for the two stilbene systems $(LiTMEDA)_2$-stilbene and $(LiPMDTA)_2$-stilbene (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine and PMDTA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine) suggest an olefinic bond lengthening of more than 0.1 Å upon complexation with two lithium atoms [6]. In addition, the stilbene molecules were found to retain the planarity of the parent hydrocarbon.

The dianion of $\Delta^{9,9'}$-bifluorene was first prepared by Schlenk and Bergmann [7] in 1920 via alkali metal reduction in diethyl ether. More recently, Cox [8] has recorded the NMR spectrum of the potassium salt of the dianion in tetrahydrofuran and determined the chemical shift for each bifluorenyl proton. Our primary goal in this work was to compare the solid state structures of the neutral hydrocarbon and the dianion in order to determine what deformations, if any, occurred in the bifluorenyl system upon reduction. Furthermore, we wished to examine the specific nature of the lithium—carbanion interaction in the bifluorenyl system, and compare this with the corresponding feature in the dilithio stilbene and monolithio fluorenyl molecular complexes. A directed covalent bonding model has been proposed to account for the lithium—carbanion orientations observed in several structural determinations of compounds containing a disolvated lithium cation and a π-delocalized carbanion [9-13], since a purely electrostatic model [11,14] does not correctly predict the geometries observed in these systems.

Experimental

A. Synthesis. A 2.15 g (6.5 mmol) sample of 9,9′-bifluorene was placed in a 250 ml three-necked flask under a nitrogen atmosphere, and 150 ml of dry hexane was added. To this was added 2 ml (13 mmol) of *N,N,N′,N′*-tetramethylethylenediamine. A 10 ml (13 mmol) sample of n-butyllithium in hexane was added to the flask via syringe while stirring at room temperature; a dark red solution immediately resulted. After addition of the n-butyllithium, stirring was stopped. The reaction mixture was brought inside an argon-filled dry box and allowed to stand 48 hours. Dark red crystals formed which were collected by filtration and dried under vacuum. The crystals were used without further purification.

B. Nuclear magnetic resonance spectrum. The nuclear magnetic resonance spectrum of $C_{26}H_{16}(N_2C_6H_{16}Li)_2$ was recorded at 44°C in benzene-d_6 on a Varian A60 spectrometer using TMS as internal standard. Singlets at δ 0.78 and 1.03 ppm have been assigned to the methyl and methylene protons, respectively, of TMEDA. Multiplets centered at δ 7.42, 7.27, 6.90, and 8.06 ppm have been assigned to the bifluorenyl protons bonded to C(1), C(2), C(3), and C(4), respectively. Assignment of chemical shift for each proton was made using the integrated intensity of each peak and by comparison with the NMR spectra of bifluorenyldipotassium [8], fluorenyllithium [15], fluorenylsodium [16,17], and fluorenylpotassium [16].

C. X-ray Analysis

1. Data collection and reduction. Crystals for X-ray analysis were sealed in thin-walled glass capillaries in an argon atmosphere because of the sensitivity of $C_{26}H_{16}(N_2C_6H_{16}Li)_2$ to oxygen and moisture. Preliminary precession photographs showed the crystals to be monoclinic with systematic absences on hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$, indicating the space group was Cc or $C2/c$. The space group $C2/c$ was subsequently used in the refinement on the basis of statistical tests and the successful solution and refinement in the centric space group. An irregularly shaped block of approximate dimensions 0.3 mm × 0.4 mm × 0.5 mm cleaved from a larger crystal was used for data collection. The crystal was mounted so that the rotation axis was coincident with the c^* axis. Twelve reflections centered on a Picker four-circle diffractometer were used in a least squares refinement of the lattice parameters and the following cell constants obtained (T = 20°C, λ = 0.71069 Å): a = 10.814(3), b = 16.717(6), c = 19.766(6) Å, and β = 102.55(2)°. The measured density, obtained by flotation in a bromobenzene/hexane mixture, was 1.10(3) g cm^{-3}. The calculated density was 1.094 g cm^{-3} for four molecules per unit cell.

Intensity data were measured using Mo-K_α radiation on an automated Picker four-circle diffractometer equipped with a graphite single-crystal monochromator. Data were collected using the $\theta - 2\theta$ scan technique with a scan rate of 1.0°/min. Stationary crystal—stationary counter background counts of 10 sec were taken at the beginning and end of each scan. A scan width of 1.8° and a take-off angle of 1.6° were employed for data collection. Several ω scans showed the typical full peak width at half height to be 0.13°, indicating that the mosaicity was acceptably low for data collection. Three standard reflections were monitored after every 60 reflections to insure crystal and counter stability. Because the background counts of the standards were observed to be drifting during the course of data collection, indicating a change of crystal centering, the crystal was optically recentered in the X-ray beam twice during data collection.

A full form of data (hkl) and hkl) was measured to $2\theta_{max}$ = 45°, giving 2749 reflections, of which 2426 were unique and 1376 classified as observed using the criterion $I_{obs} \geqslant 3\sigma_c(I)$, 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 the background counts. Due to the irregular crystal shape and the small value for the linear absorption coefficient (μ = 0.68 cm^{-1}), no absorption correction was made. The remainder of the data collection details are the same as previously reported [10].

2. Solution and refinement of the structure. The structure of $C_{26}H_{16}(N_2C_6H_{16}Li)_2$ was solved using direct methods (symbolic addition procedure) with the symbolic program MULTAN [18]. The E-map generated from the set of phases with the highest figure of merit yielded the positions of all thirteen unique bifluorenyl carbon atoms, the two TMEDA nitrogen atoms, and the four TMEDA methyl carbon atoms. A difference Fourier calculated at this point revealed the lithium position and two somewhat poorly defined positions for the TMEDA methylene carbon atoms. The R factor was $R_1 = \Sigma F_o—F_c/\Sigma F_o = 0.291$. Full matrix least squares refinement using the program ORFLSD gave at isotropic convergence an R factor of $R_2 = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2} = 0.176$. The hydrogen atoms were then added at the calculated positions using the program HYGEN. Each hydrogen atom was given an isotropic thermal parameter equal to that of its parent carbon atom and placed 1.0 Å from that atom. Further isotropic refinement of the non-hydrogen atoms, and conversion from unit weights to a statistical weighting scheme ($k = 0.03$) previously defined [9], gave $R_2 = 0.152$. Continued refinement after conversion to anisotropic thermal parameters led to final values of R_1 and R_2: $R_1 = 0.053$ (observed data), $R_2 = 0.064$ (all data), and $ERF = [\Sigma w(F_o - F_c)^2/(NO - NV)]^{1/2} = 1.79$ where NO = number of observations and NV = number of variables. A final difference Fourier showed peaks of 0.24, 0.22, and 0.21 e A^{-3} located near the TMEDA methylene carbon atoms, one TMEDA nitrogen atom, and one TMEDA methyl carbon atom, respectively. A test of the weighting scheme showed no significant variation of $w(F_o - F_c)^2$ with the magnitudes of the F_{obs} or increasing $\sin \theta/\lambda$. During anisotropic refinement, not all non-hydrogen atom thermal and positional parameters could be varied at once, due to core storage limitations. Parameters for all thirteen bifluorenyl carbon atoms, the two TMEDA nitrogen atoms, the lithium atom, and four of the six TMEDA carbon atoms were varied in any one cycle. The scattering factors for C°, N°, and Li° used in refinement were taken from the compilation of Hanson et al. [19] and those for the hydrogen atoms are the best spherical form factors of Stewart et al. [20].

TABLE 1

POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN BIFLUORENYL BIS(LITHIUM TMEDA)

Atom	x	y	z
C(1)	0.0080(2)[a]	0.2433(2)	0.1636(1)
C(2)	0.0456(3)	0.2906(2)	0.1146(1)
C(3)	0.1411(3)	0.2653(2)	0.0812(1)
C(4)	0.1989(3)	0.1929(2)	0.0965(1)
C(5)	0.2979(3)	0.0140(2)	0.1571(2)
C(6)	0.3238(3)	—0.0560(2)	0.1935(2)
C(7)	0.2541(4)	—0.0783(2)	0.2427(2)
C(8)	0.1579(3)	—0.0304(2)	0.2554(1)
C(9)	0.0456(2)	0.1064(2)	0.2267(1)
C(10)	0.0661(2)	0.1682(2)	0.1807(1)
C(11)	0.1625(2)	0.1426(2)	0.1449(1)
C(12)	0.2040(3)	0.0648(2)	0.1702(1)
C(13)	0.1313(2)	0.0498(2)	0.2201(1)
AC(1)	0.1202(4)	0.0926(3)	0.4780(2)
AC(2)	0.1702(5)	—0.0308(3)	0.4377(2)
AC(3)	0.3268(4)	0.0714(4)	0.4606(2)
AC(4)	0.3865(4)	0.1236(4)	0.4305(2)
AC(5)	0.3445(4)	0.2456(3)	0.3709(3)
AC(6)	0.4077(3)	0.1353(3)	0.3165(2)
N(1)	0.1945(2)	0.0541(2)	0.4352(1)
N(2)	0.3353(2)	0.1602(2)	0.3655(1)
Li	0.1562(5)	0.1091(3)	0.3393(2)

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

TABLE 2

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN BIFLUORENYL BIS(LITHIUM TMEDA)

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0099(3)	0.0037(1)	0.0022(1)	−0.0001(2)	0.0007(1)	0.0002(1)
C(2)	0.0152(4)	0.0038(1)	0.0030(1)	−0.0001(2)	0.0012(2)	0.0005(1)
C(3)	0.0162(5)	0.0056(2)	0.0027(1)	−0.0021(2)	0.0023(2)	0.0004(1)
C(4)	0.0109(4)	0.0057(2)	0.0027(1)	−0.0012(2)	0.0016(2)	−0.0006(1)
C(5)	0.0111(4)	0.0057(2)	0.0033(1)	0.0010(2)	0.0009(2)	−0.0013(1)
C(6)	0.0131(4)	0.0065(2)	0.0049(2)	0.0030(3)	0.0011(2)	−0.0016(1)
C(7)	0.0175(5)	0.0043(2)	0.0042(1)	0.0031(2)	−0.0002(2)	−0.0002(1)
C(8)	0.0131(4)	0.0036(1)	0.0031(1)	0.0011(2)	0.0004(2)	0.0001(1)
C(9)	0.0080(3)	0.0033(1)	0.0020(1)	0.0000(2)	0.0005(1)	0.0000(1)
C(10)	0.0074(3)	0.0037(1)	0.0020(1)	−0.0003(2)	0.0001(1)	0.0004(1)
C(11)	0.0084(3)	0.0046(1)	0.0022(1)	−0.0006(2)	0.0007(1)	−0.0004(1)
C(12)	0.0089(3)	0.0046(2)	0.0023(1)	0.0007(2)	0.0006(1)	−0.0008(1)
C(13)	0.0089(3)	0.0038(1)	0.0022(1)	0.0003(2)	0.0001(1)	−0.0004(1)
AC(1)	0.0256(7)	0.0109(3)	0.0035(1)	0.0045(4)	0.0019(2)	0.0014(2)
AC(2)	0.0424(10)	0.0080(3)	0.0046(2)	0.0018(4)	0.0040(3)	0.0019(2)
AC(3)	0.0132(6)	0.0221(5)	0.0068(2)	−0.0005(4)	−0.0015(3)	0.0078(3)
AC(4)	0.0165(6)	0.0204(5)	0.0049(2)	−0.0053(5)	−0.0025(3)	0.0032(3)
AC(5)	0.0179(6)	0.0073(3)	0.0157(4)	−0.0001(3)	0.0022(4)	−0.0017(3)
AC(6)	0.0129(5)	0.0154(4)	0.0051(2)	−0.0011(3)	0.0011(2)	−0.0033(2)
N(1)	0.0141(3)	0.0068(2)	0.0032(1)	0.0016(2)	0.0007(1)	0.0014(1)
N(2)	0.0117(3)	0.0059(1)	0.0032(1)	0.0001(2)	0.0003(1)	−0.0003(1)
Li	0.0111(6)	0.0064(3)	0.0028(2)	0.0000(3)	0.0000(2)	0.0003(2)

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

TABLE 3

INTERATOMIC DISTANCES (Å) FOR THE NON-HYDROGEN ATOMS IN BIFLUORENYL BIS(LITHIUM TMEDA)

Atoms	Distance	Atoms	Distance
C(1)—C(2)	1.378(3)[a]	C(9)—C(13)	1.435(3)
C(1)—C(10)	1.413(3)	N(1)—AC(1)	1.439(4)
C(2)—C(3)	1.405(4)	N(1)—AC(2)	1.447(5)
C(3)—C(4)	1.365(4)	N(1)—AC(3)	1.439(3)
C(4)—C(11)	1.394(4)	N(2)—AC(4)	1.422(2)
C(5)—C(6)	1.369(4)	N(2)—AC(5)	1.433(5)
C(5)—C(12)	1.390(4)	N(2)—AC(6)	1.433(4)
C(6)—C(7)	1.404(5)	AC(3)—AC(4)	1.304(6)
C(7)—C(8)	1.379(4)	Li—C(9)	2.287(5)
C(8)—C(13)	1.407(4)	Li—C(9)′	2.287(5)
C(9)—C(9)′	1.487(5)	Li—C(10)′	2.549(6)
C(9)—C(10)	1.426(3)	Li—C(13)	2.565(6)
C(10)—C(11)	1.445(3)	Li—N(1)	2.066(5)
C(11)—C(12)	1.431(4)	Li—N(2)	2.077(6)
C(12)—C(13)	1.436(4)		

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

TABLE 4

BOND ANGLES (deg) FOR THE NON-HYDROGEN ATOMS IN BIFLUORENYL BIS(LITHIUM TMEDA)

Atoms	Angle	Atoms	Angle
C(2)—C(1)—C(10)	119.6(2)[a]	C(5)—C(12)—C(11)	132.6(3)
C(1)—C(2)—C(3)	121.1(3)	C(5)—C(12)—C(13)	120.2(3)
C(2)—C(3)—C(4)	120.7(3)	C(11)—C(12)—C(13)	107.1(2)
C(3)—C(4)—C(11)	120.2(3)	C(8)—C(13)—C(9)	131.7(3)
C(6)—C(5)—C(12)	119.9(3)	C(8)—C(13)—C(12)	118.6(3)
C(5)—C(6)—C(7)	120.7(3)	C(9)—C(13)—C(12)	109.6(2)
C(6)—C(7)—C(8)	120.8(3)	AC(1)—N(1)—AC(2)	106.9(3)
C(7)—C(8)—C(13)	119.8(3)	AC(1)—N(1)—AC(3)	110.2(4)
C(10)—C(9)—C(13)	106.5(2)	AC(2)—N(1)—AC(3)	111.0(4)
C(1)—C(10)—C(11)	118.5(2)	AC(4)—N(2)—AC(5)	110.7(4)
C(9)—C(10)—C(11)	109.1(2)	AC(4)—N(2)—AC(6)	108.8(3)
C(1)—C(10)—C(9)	132.4(2)	AC(5)—N(2)—AC(6)	107.5(3)
C(4)—C(11)—C(10)	119.9(3)	N(1)—AC(3)—AC(4)	121.8(4)
C(4)—C(11)—C(12)	132.4(3)	N(2)—AC(4)—AC(3)	124.5(4)
C(10)—C(11)—C(12)	107.7(2)	N(1)—Li—N(2)	88.0(2)

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

The final positional and thermal parameters for the non-hydrogen atoms are contained in Tables 1 and 2, respectively. Bond distances and angles are given in Tables 3 and 4, respectively*.

Discussion

The molecular structure of $\Delta^{9,9'}$-bifluorenyl bis(lithium TMEDA) consists of a bifluorene moiety bound to two lithium atoms, each of which also has one TMEDA molecule coordinated to it (Fig. 1). Only one half of the molecule is crystallographically unique, as a crystallographic twofold axis bisects the C(9)—C(9)′ bond and is perpendicular to a vector drawn between the two lithium atoms. The coordination sphere of two tertiary amine nitrogen atoms and one unsaturated organic anion around each three-coordinate lithium atom is thus the same as found in previously determined unsaturated organolithium structures [11]. The arrangement of the lithium atom with respect to the unsaturated group is, however, different than that in fluorenyllithium bisquinuclidine [9]. Each lithium atom lies on a bisector of the C(9)—C(9)′ bond and is 2.287(5) Å away from C(9) and C(9)′, 2.565(6) Å away from C(13) and, because of rotation from coplanarity of the two fluorenyl rings, is 2.549(6) Å away from C(10)′. As in all other unsaturated organolithium structures which have been studied to date, each lithium atom is in a position corresponding to a nodal surface of the highest occupied molecular orbital (HOMO) of the dianion (Fig. 2) [21]. The LiN_2 fragment is aligned in such a way as to allow a σ-bonding interaction between the

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* The table of structure factors has been deposited as NAPS Document No. 02635 (18 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

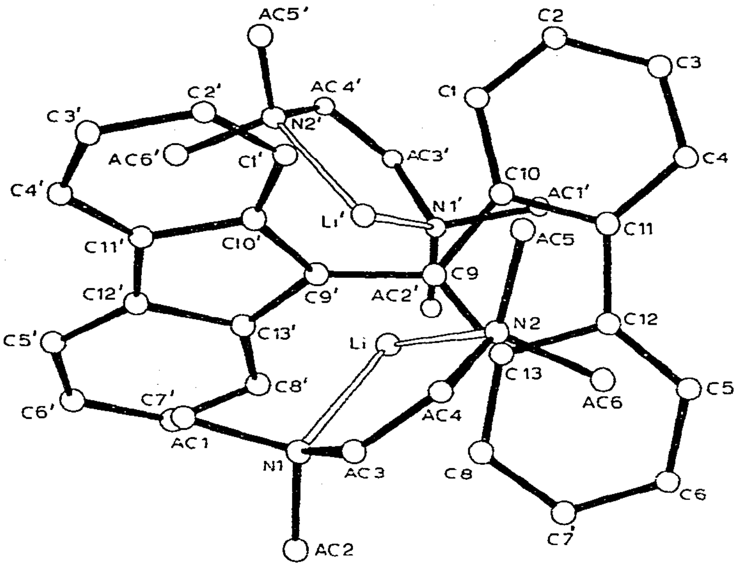


Fig. 1. The molecular structure of bifluorenyl bis(lithium TMEDA).

lithium 2*s* and 2*p* orbitals and combinations of ring carbon *s* and p_z orbitals making up lower energy dianion molecular orbitals. The LiN_2 fragment is also positioned in the proper orientation with respect to the symmetry of the HOMO of the carbanion to permit an interaction between a lithium 2*p* orbital and the *p*

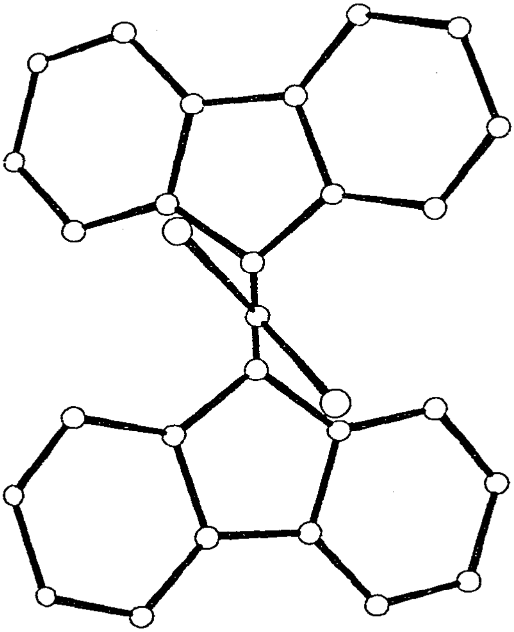


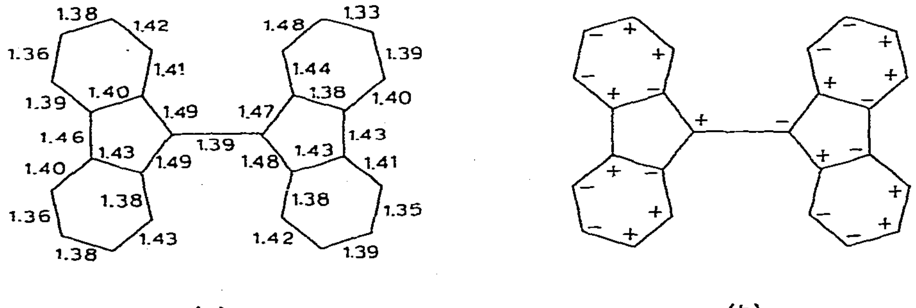
Fig. 2. Orientation of the LiN_2 plane relative to bifluorene, as viewed down the Li—Li' vector.

orbitals on C(13) and C(10)′ which are perpendicular to the fluorenyl ring planes. Similarly, Li′ can bond with C(10) and C(13)′. The rules previously proposed [11-13] are thus seen to be followed in this structure; each lithium atom is in a position corresponding to a nodal surface of the HOMO of the dianion, and is closest to C(9) and C(9)′, the two carbon atoms making the largest contributions to the HOMO [11,21].

It should be pointed out, however, that a simple electrostatic bonding model [14] also would predict the same positions for the lithium atoms, relative to the carbanion, as was experimentally determined. In addition, the orientations of the TMEDA molecules are consistent with minimizing non-bonded interactions with each fluorenyl ring. Therefore, a description of the molecular structure of this compound does not require a directed covalent contribution to the bonding.

The structural parameters determined for the carbanion geometry agree well with qualitative predictions based on the HOMO in the dianion. The central five carbon rings of each fluorenyl ring make an angle of 48.0(5)° with respect to each other, while the torsional angle around the C(9)—C(9)′ bond is 47.5(5)°. This represents an increase from the 42° angle observed in $\Delta^{9,9'}$-bifluorene [4]. The C(9)—C(9)′ bond distance has increased from 1.39(2) Å in $\Delta^{9,9'}$-bifluorene [4] to 1.487(5) Å in the dianion, as predicted by the signs and magnitudes of the coefficients of the HOMO of the carbanion (Fig. 3) [21]. We note that the increase in the C(9)—C(9)′ distance should lead to a decrease in the non-bonded interactions between ring hydrogen atoms.

The carbon—carbon bond distances in each six-membered outer ring of the fluorenyl ring alternate between long and short, in agreement with the signs of the coefficients of the HOMO of the dianion. The same alternation of distances and symmetry occurred in fluorenylpotassium TMEDA [22], but was not as pronounced in fluorenyllithium bisquinuclidine [9]. Distances between atoms which are roughly chemically equivalent in the two six-membered rings, the C(1)—C(2) and C(7)—C(8) distances, for example, are within two standard deviations or less of being equal; each fluorenyl ring roughly shows two-fold symmetry. The carbon—carbon distances in the five-membered ring average 1.435(3) Å in the bifluorenyl dianion, while in fluorenylpotassium and fluorenyllithium they are 1.418(4) Å and 1.427(7) Å, respectively.



(a) (b)

Fig. 3. (a) Bond lengths (Å) in $\Delta^{9,9'}$-bifluorene [4]. (b) Signs of the coefficients of the HOMO of the dianion of $\Delta^{9,9'}$-bifluorene [21].

TABLE 5

BEST WEIGHTED LEAST-SQUARES PLANES FOR BIFLUORENYL BIS(LITHIUM TMEDA)

Atoms in plane	Equation of plane[a,b]
C(1), C(2), C(3), C(4), C(5), C(6), C(7) C(8), C(9), C(10), C(11), C(12), C(13)	$-0.5400x - 0.4310y - 0.7229z + 3.6784 = 0$

Atom	Deviation (Å) from plane
C(1)	−0.023(3)
C(2)	−0.014(3)
C(3)	−0.002(3)
C(4)	0.005(3)
C(5)	0.011(3)
C(6)	−0.060(4)
C(7)	−0.064(4)
C(8)	0.006(3)
C(9)	0.009(2)
C(10)	−0.021(3)
C(11)	0.016(3)
C(12)	0.042(3)
C(13)	0.044(3)
Li	−1.966(5)

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

The fluorenyl ring deviates slightly from planarity (see Table 5). The central five-membered ring (C(9), C(10), C(11), C(12), C(13); Plane A) and the outer six-membered rings (C(1), C(2), C(3), C(4), C(10), C(11); Plane B. C(5), C(6), C(7), C(8), C(12), C(13); Plane C) are each essential planar, however, the dihedral angle is 1.1(5)° between planes A and B, and 4.0(5)° between A and C. Planes B and C are tipped in opposite directions with respect to the five-membered ring. Non-planarity was also of the fluorenyl ring seen in fluorenyllithium [9] and fluorenylpotassium [22], and the dihedral angles found in those compounds are similar to the values observed here.

The Li—N(1) and Li—N(2) bond lengths are 2.066(5) and 2.077(5) Å, respectively, and the N(1)—Li—N(2) bond angle is 88.0(2)°; the bond angle is similar to that seen in other structures containing a lithium TMEDA moiety [10-13]. However, the average lithium—nitrogen bond length of 2.072(5) Å is among the shortest thus far observed in an aryllithium TMEDA structure; only the 2.064(8) Å average lithium—nitrogen distance found in acenaphthene bis(lithium TMEDA) [23] is shorter. In the absence of steric effects, a correlation between the pK_a of the acidic proton of the parent hydrocarbon and the resultant lithium—nitrogen distance has been noted with the most stable carbanion exhibiting the shortest lithium—nitrogen distance. In the case of bifluorenyl bis(lithium TMEDA), it is interesting to note that the lithium—nitrogen distance is shorter than those observed in naphthalene bis(lithium TMEDA) (2.114(9) Å) [10] and anthracene bis(lithium TMEDA) [13] (2.111(6) and 2.088(6) Å). From polarographic $E_{1/2}$ values [2], it is expected that the bifluorenyl dianion would be the most stable of the three, and the distances found parallel this stability. Caution still should

TABLE 6A

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) ALONG THE PRINCIPAL AXES R_i FOR BIFLUORENYL BIS(LITHIUM TMEDA)

Atom	R_1	R_2	R_3
C(1)	0.203(4)	0.232(4)	0.239(4)
C(2)	0.214(5)	0.252(4)	0.296(4)
C(3)	0.204(5)	0.265(4)	0.324(4)
C(4)	0.217(4)	0.239(4)	0.295(4)
C(5)	0.217(5)	0.245(4)	0.317(4)
C(6)	0.222(5)	0.280(5)	0.367(5)
C(7)	0.215(5)	0.268(4)	0.361(4)
C(8)	0.216(5)	0.238(4)	0.290(4)
C(9)	0.191(4)	0.217(4)	0.219(4)
C(10)	0.178(4)	0.220(4)	0.234(4)
C(11)	0.196(4)	0.221(4)	0.259(4)
C(12)	0.194(4)	0.220(4)	0.274(4)
C(13)	0.190(4)	0.224(4)	0.251(4)
AC(1)	0.245(5)	0.341(5)	0.436(5)
AC(2)	0.254(6)	0.360(6)	0.491(6)
AC(3)	0.216(6)	0.316(6)	0.622(7)
AC(4)	0.234(6)	0.339(6)	0.571(7)
AC(5)	0.315(6)	0.319(6)	0.555(7)
AC(6)	0.259(5)	0.291(5)	0.489(6)
N(1)	0.218(4)	0.292(3)	0.329(4)
N(2)	0.230(3)	0.274(3)	0.293(4)
Li	0.214(7)	0.273(6)	0.303(7)

TABLE 6B

POSITIONAL PARAMETERS AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS IN BIFLUORENYL BIS(LITHIUM TMEDA)

Atom	x	y	z	B^a
H(1)	−0.0607	0.2620	0.1879	3.69
H(2)	0.0052	0.3446	0.1029	4.96
H(3)	0.1663	0.2996	0.0447	4.95
H(4)	0.2676	0.2779	0.0723	4.81
H(5)	0.3493	0.0278	0.1216	5.08
H(6)	0.3943	−0.0900	0.1862	5.95
H(7)	0.2758	−0.1295	0.2676	6.07
H(8)	0.1077	−0.0476	0.2905	4.89
AH(11)	0.0299	0.0824	0.4599	8.65
AH(12)	0.1467	0.0734	0.5261	8.65
AH(13)	0.1377	0.1520	0.4763	8.65
AH(21)	0.0777	−0.0401	0.4204	10.10
AH(22)	0.2194	−0.0590	0.4077	10.10
AH(23)	0.1951	−0.0494	0.4862	10.10
AH(31)	0.3713	0.0166	0.4542	12.09
AH(32)	0.3375	0.0807	0.5101	12.09
AH(41)	0.3990	0.1706	0.4657	11.94
AH(42)	0.4705	0.1028	0.4281	11.94
AH(51)	0.3122	0.2712	0.3269	12.39
AH(52)	0.3008	0.2646	0.4078	12.39
AH(53)	0.4390	0.2591	0.3866	12.39
AH(61)	0.3738	0.1586	0.2700	9.10
AH(62)	0.4982	0.1530	0.3322	9.10
AH(63)	0.4067	0.0751	0.3128	9.10

[a] The form of the isotropic thermal parameter is $\exp[-B(\sin^2 \theta/\lambda^2)]$.

be exercised in attributing the observed distances solely to anion stability.

The root-mean-square amplitudes of vibration of the TMEDA carbon atoms are quite large (Table 6) and the carbon—carbon bond length of 1.304(6) Å between the TMEDA methylene carbon atoms is chemically unreasonable. These results are probably due to the carbon anisotropic thermal parameters compensating for either a dynamic disorder in the TMEDA molecule, similar to that observed by Brooks et al. for the TMEDA in triphenylmethyllithium TMEDA [24], or a static disorder of the TMEDA molecule with the two orientations very close to each other. Since the bifluorene portion of the complex determines the packing in the crystal, the TMEDA molecules have a relatively large space in which to move. Thus, the behavior observed by Brooks probably exists here also, and the thermal parameters have for the most part compensated for this vibration. No attempt was made to refine the structure using a disordered TMEDA molecule, and since there was no correlation of thermal and positional parameters for the methylene carbon atoms with those of other atoms, it is felt that the one short carbon—carbon distance does not effect the basic molecular geometry found or other distances and their standard deviations. Brooks et al. [24] made the same conclusion in a careful analysis of the refinement of triphenylmethyllithium TMEDA.

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