New acenaphthene-1,2-diimine and its reduction to the tetraanion. Molecular structures of 1,2-bis[(trimethylsilyl)imino]acenaphthene and its lithium derivatives

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1,2-Bis[(trimethylsilyl)imino]acenaphthene (**1**) was synthesized by the reaction of acenaphthenequinone with $(Me_3Si)_2NLi$ in toluene followed by treatment of the reaction product with trimethylchlorosilane. The dianionic derivative $[(tms\text{-}BIAN)Li_2]_2$ (**3**) was obtained as the final product by reduction of compound **1** with lithium in toluene, whereas reduction in diethyl ether afforded the tetraanion $[(tms\text{-}BIAN)Li_4(Et_2O)_3]_2$ (**5**). The formation of the paramagnetic mono- and trianions in solution was confirmed by ESR spectroscopy. Compounds **3** and **5** were isolated in the crystalline state and characterized by elemental analysis, IR spectroscopy, and NMR spectroscopy. The crystal structures of **1**, **3**, and **5** were established by X-ray diffraction.

Key words: lithium, diimines, reduction, crystal structure, X-ray diffraction, ESR.

In the last decade, acenaphthene-1,2-diimines (BIAN) have been widely used as ligands in coordination chemistry. Transition metal complexes with diimine ligands are efficient catalysts for alkyne hydrogenation,[1] carbon—carbon bond formation,[2] cycloisomerization,[3] hydrosilylation,[4] polymerization of alkenes[5] and acrylic monomers,[6] and copolymerization of CO_2 and methylenecyclopropene,[7] ethylene, norbornene,[8] and styrene.[9] Acenaphthenediimine complexes of transition metals (Brookhart catalysts) are the most efficient olefin polymerization catalysts.[10] The π-acceptor properties of acenaphthene-1,2-diimines in metal complexes induce an electron deficiency at the metal atom, which is responsible for high reactivity of these complexes toward organic compounds.

Earlier, we have demonstrated that main-group metals, unlike transition metals, can form complexes with different anionic forms of BIAN ligands. We used primarily 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN), which shows variable oxidation states in complexes with main-group metals. Diimine dpp-BIAN can be reduced with alkali metals in ethereal media to the mono-, di-, tri-, and tetraanions to form the $[(dpp\text{-}BIAN)M_n(Et_2O)_n]$ salts (M = Li or Na; n = 1—4).[11] In THF, alkaline-earth metals reduce dpp-BIAN only to the dianion to give the monomeric $(dpp\text{-}BIAN)M(THF)_n$ complexes (M = Mg, Ca, Sr, or Ba; n = 2—4).[12] Reduction of dpp-BIAN with aluminum metal in the presence of halides in toluene or Et_2O affords the radical-anionic compound $(dpp\text{-}BIAN)AlCl_2$ and the dianionic products $(dpp\text{-}BIAN)AlI(Et_2O)$ and $(dpp\text{-}BIAN)AlCl(Et_2O)$, respectively.[13] We synthesized aluminum alkyl complexes with both the radical anion and the dianion of dpp-BIAN by the metathesis reactions of the corresponding sodium derivatives of dpp-BIAN with alkylaluminum halides.[14] The metathesis of sodium salts of three different acenaphthene-1,2-diimines with $GeCl_2$ gave the germanium(II) compounds (BIAN)Ge [15] and (dpp-BIAN)GeCl.[16]

The $(dpp\text{-}BIAN)Mg(thf)_3$ complex acts as a one-electron reducing agent for organic halides[17] and aromatic ketones.[18] The reactions of $(dpp\text{-}BIAN)Mg(thf)_3$ with compounds containing a mobile hydrogen atom, for example, with aliphatic ketones,[19] nitriles,[12b] or phenylacetylene,[20] involve the addition of these substrates to the complex through protonation of one nitrogen atom of the dpp-BIAN ligand to give, respectively, enolate, ketimide, and phenylethynyl derivatives.

However, only acenaphthene-1,2-diimines containing aryl substituents at the nitrogen atoms have been used earlier[21] because the synthesis of *N*,*N*-bis(alkyl)imino-

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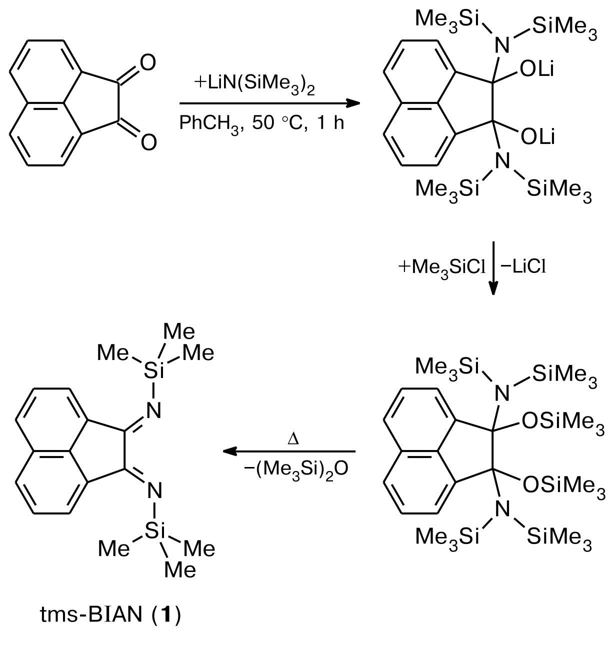
acenaphthenes presents difficulties. The reactions of primary alkylamines with acenaphthenequinone proceed under severe conditions and stop at the condensation product of only one carbonyl group. Recently,[22] the synthesis of acenaphthene-1,2-diimine containing alkyl substituents at the nitrogen atoms has been documented. *N*,*N*-Bis(cyclopropyl)iminoacenaphthene was prepared by transamination of bis(arylimino)acenaphthene with cyclopropylamine. Unlike acenaphthenequinone, glyoxal derivatives readily form diimines in the reactions with both anilines and primary aliphatic amines.

In the present study, we synthesized the first acenaphthene-1,2-diimine containing silyl substituents at the nitrogen atoms and obtained products of its reduction with lithium metal both in solvating (Et_2O and THF) and nonsolvating (toluene) solvents.

Results and Discussion

Synthesis of 1,2-bis[(trimethylsilyl)imino]acenaphthene (tms-BIAN, 1). We synthesized trimethylsilyl-substituted acenaphthene-1,2-diimine using the approach, which has been applied earlier[23] to the synthesis of Me_3Si-substituted α-diimines from α-diketones. This method is based on the addition of lithium or sodium bis(trimethylsilyl)amides at the carbonyl groups of diketones followed by elimination of hexamethyldisiloxane from the addition products under the action of Me_3SiCl. The target product, *viz*., 1,2-bis[(trimethylsilyl)imino]acenaphthene (**1**), was synthesized according to Scheme 1.

Scheme 1



Compound **1** was isolated from the reaction mixture by vacuum sublimation. Recrystallization of the sublimed product from hexane afforded compound **1** as orange needle-like crystals. Unlike bis(arylimino)acenaphthenes, diimine **1** is unstable in air because, apparently, of N—Si bond hydrolysis. Compound **1** was characterized by elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The crystal structure of **1** was established by X-ray diffraction.

Reduction of diimine 1 with lithium metal. Stirring of diimine **1** with an excess of lithium in Et_2O at room temperature for 1 h was accompanied by a stepwise change in the color of solution, which is indicative of reduction of diimine **1** with the successive formation of its anionic forms. Reduction of diimine **1** occurs more rapidly compared to that of Ar-substituted acenaphthenediimines, for example, of dpp-BIAN.[11b] The monitoring of reduction of diimine **1** by NMR and ESR spectroscopy proved the successive formation of the following four anions in this reaction: (tms-BIAN)$^-$ (**2**$^-$), (tms-BIAN)$^{2-}$ (**3**$^{2-}$), (tms-BIAN)$^{3-}$ (**4**$^{3-}$), and (tms-BIAN)$^{4-}$ (**5**$^{4-}$). After stirring in diethyl ether for 1 h, the color of the reaction mixture ceased to change, which is evidence that reduction was completed. Decantation of the resulting green solution from unconsumed lithium and removal of the solvent *in vacuo* afforded crystals of the tetralithium derivative $[(\text{tms-BIAN})Li_4(Et_2O)_3]_2$ (**5**), which were characterized by elemental analysis, ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR spectroscopy, and IR spectroscopy. The structure of compound **5** was established by X-ray diffraction. Reduction of diimine **1** with lithium in toluene is not so deep and stops at the formation of the dilithium derivative $[(\text{tms-BIAN})Li_2]_2$ (**3**), which was also characterized by spectroscopic methods and X-ray diffraction. The paramagnetic monoanions (**2**$^-$) and trianions (**4**$^{3-}$) were not isolated from the solution. However, their formation was established based on the characteristic parameters of ESR spectra.

The ESR spectra of paramagnetic derivatives **2** and **4** are shown in Figs 1 and 2, respectively. The beginning of

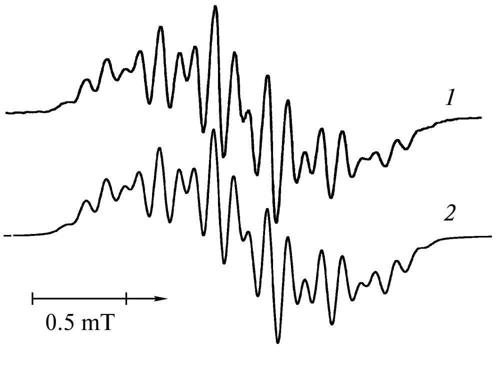


Fig. 1. ESR spectrum of the radical anion (tms-BIAN)$^-$ (**2**$^-$) in THF at 255 K (*1*) and its computer simulation (*2*).

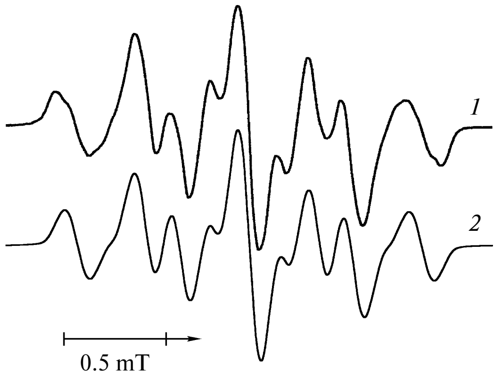


Fig. 2. ESR spectrum of the radical trianion (tms-BIAN)$^{3-}$ (**4**$^{3-}$) in THF at 293 K (*1*) and its computer simulation (*2*).

reduction was evidenced by the appearance of the red color of the reaction mixture accompanied by the appearance of the ESR spectrum of the lithium salt of the radical anion (tms-BIAN)$^{\bullet -}$ (see Fig. 1, curve *1*). The hyperfine structure of the spectrum is attributed to the coupling of the unpaired electron with the ^{7}Li isotope, two equivalent ^{14}N nuclei, and two pairs of the equivalent protons of the naphthalene moiety (g = 2.0032, A_N = 0.29, A_H = 0.11, A_H = 0.106, A_{Li} = 0.85 mT). Upon further stirring, the solution turned blue and a new complex multiplet appeared (total width was 3.5 mT, the linewidth was 0.1 mT). We failed to interpret this signal. However, in our opinion, this signal is attributed to association of the dianion that is generated in the second step of reduction with the radical anion present in the mixture. In the [(tms-BIAN)$^{2-}$Li$_3$(tms-BIAN)$^-$]$^{3-}$ associate, the unpaired electron is delocalized over two ligands and three lithium atoms, resulting in the appearance of a multiline spectrum of this associate.

In the course of further stirring, the blue color of the reaction mixture gradually changed to green, and the second ESR spectrum disappeared, which is indicative of the formation of the diamagnetic dianion (tms-BIAN)$^{2-}$. The latter was characterized by ^{1}H NMR spectroscopy (see below). The dianion is gradually reduced to give the paramagnetic radical trianion, whose formation was observed by ESR spectroscopy (see Fig. 2). Since reduction of the dianion is accompanied by occupation of the molecular orbital, which is composed primarily of the p$_z$-atomic orbitals of the carbon atoms of the naphthalene moiety, the spin density in the trianion is distributed over the naphthalene π system. For example, the ESR spectrum of the trianion shows a hyperfine coupling constant (g = 2.0029, A_H = 0.5, A_H = 0.34, A_H = 0.036, A_N = 0.035 mT) due to splitting of the unpaired electron on three pairs of protons of the six-membered rings, the hyperfine coupling constant with the nitrogen atoms being substantially decreased compared to that of the radical monoanion.

The ^{1}H NMR spectra of diamagnetic compounds **1**, **3**, and **5** are presented in Fig. 3. All three spectra show three multiplets (two doublets and a pseudotriplet) for the aromatic protons and a singlet of the Me$_3$Si group. The chemical shifts of the protons in the spectra of **1**, **3**, and **5**

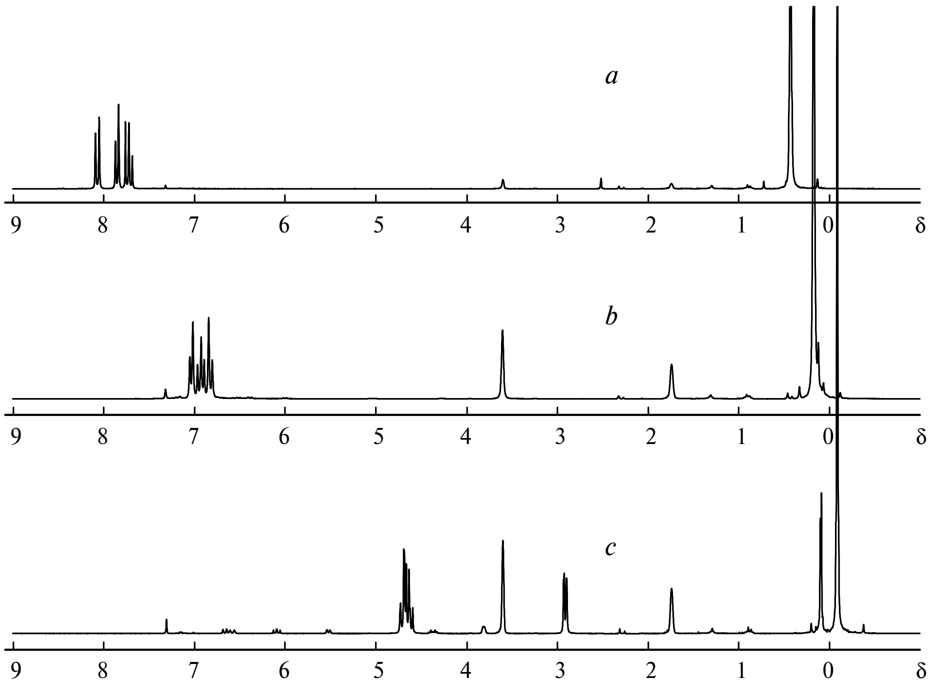


Fig. 3. ^{1}H NMR spectra of compounds **1** (*a*), **3** (*b*), and **5** (*c*) (200 MHz, THF, 293 K).

Table 1. ^{1}H NMR spectroscopic data for compounds **1**, **3**, and **5** (200 MHz, THF, 293 K)

Group	δ		
	1	**3**	**5**
CH arom.	8.07,[a] 7.85,[a] 7.72[b]	7.03,[a] 6.92,[b] 6.82[a]	4.71,[a] 4.63,[b] 2.91[a]
SiMe	0.43	0.17	–0.09

[a] Doublet.

[b] Pseudotriplet.

are given in Table 1. The signal for the protons of the aromatic rings in the spectrum of the dianion is shifted upfield by ~1 ppm compared to that observed in the spectrum of diimine **1**. The dramatically strong upfield shifts of the signals for the aromatic protons (by ~3.5 ppm for two signals and by 5 ppm for the third signal) are observed in the spectrum of the tetraanion compared to the corresponding signals in the spectrum of the dianion (see Table 1).

As can be seen from the NMR spectroscopic data, two-electron reduction of diimine **1** leads to localization of the negative charge predominantly on the diimine moiety of the dianion, to be more precisely, on the nitrogen atoms. The lowest unoccupied molecular orbital of the dianion is filled in the tetraanion. This orbital is localized on the naphthalene moiety of the molecule. This is responsible for the strong upfield shift of the signals for the protons of the naphthalene moiety. The signal for the protons of the Me_3Si group is monotonically shifted upfield in the series of **1**, **3**, and **5**. In virtually all Ar-substituted acenaphthene-1,2-diimines, the planes of the Ph rings at the nitrogen atoms are orthogonal to the plane of the diimine moiety. This hinders the conjugation of the π systems of these substituents with both the diimine π system and the lone electron pairs of the nitrogen atoms, which are orthogonal to the plane of the diimine system in the dianion. In diimine tms-BIAN, the pairs of the nitrogen atoms in the dianion can be involved in the n—d conjugation with the d orbitals of the silicon atom. The strength of this conjugation can be estimated by analyzing the structural parameters of **1**, **3**, and **5**.

Molecular structures of compounds 1, 3, and 5. The structures of compounds **1**, **3**, and **5** were established by X-ray diffraction study of single crystals grown from hexane (**1** and **3**) or diethyl ether (**5**). The structures of **1**, **3**, and **5** are shown in Figs 4, 5, and 6, respectively. The crystallographic data, details of X-ray data collection, and characteristics of the structure refinement are given in Table 2. Selected bond lengths and bond angles are listed in Tables 3, 4, and 5, respectively.

In the crystalline state, diimine **1** exists as the *E,Z* isomer. The structures of two acenaphthene-1,2-diimines are known. In the crystalline state, 1,2-bis[(2-biphenyl)imino]acenaphthene[24] also exists as the *E,Z* isomer, whereas 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene, which is most often used as the ligand,[25] exists as the *E,E* isomer. Unlike the latter compound, **1** has no mirror plane passing along the C(4)—C(9) bond perpendicular to the plane of the naphthalene moiety of the molecule. In this case, the signals for the aromatic protons and the Me_3Si groups in the ^{1}H NMR spectra would be expected to be nonequivalent. However, the ^{1}H NMR spectra in $CDCl_3$, C_6D_6, or THF-d_8 (see the Experimental section) show only three signals for the aromatic protons and one signal for the protons of the methyl groups, which is indicative of the presence of a mirror plane in the molecule of compound **1** in solution. Presumably, compound **1** exists as the *E,E* isomer in solution. In spite of the difference in the positions of the Me_3Si substituents at the double carbon—nitrogen bonds, the C—N and Si—N distances are virtually identical (see Table 3). The C—N bond lengths (1.2702(19) and 1.2637(19) Å) are similar to the corresponding distances in 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (both bond lengths are 1.282(4) Å).[25] The C(1)—C(2) distance (1.5478(18) Å) in the structure of **1** corresponds to the single carbon—carbon bond length. The bond angle at the N(1) atom is similar to that at the N(2) atom (133.79(10) and 132.74(11)°, respectively).

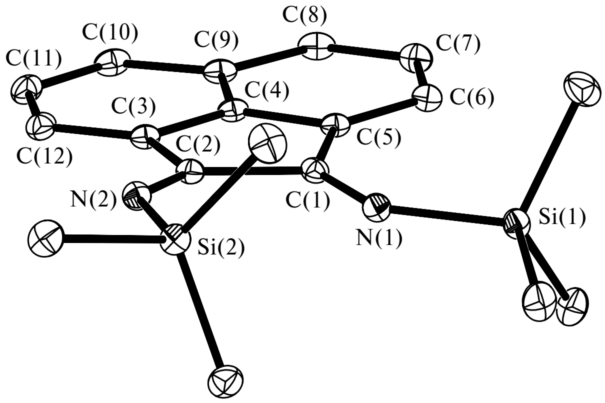


Fig. 4. Molecular structure of tms-BIAN (**1**). The hydrogen atoms are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

In the crystalline state, compound **3** exists as a dimer formed through interactions between the lithium and nitrogen atoms of two adjacent molecules. Although each fragment in the dimer is crystallographically independent, the geometric parameters of these fragments are similar. Because of this, we analyzed the bond lengths and bond angles only in one (tms-BIAN)Li_2 fragment in compound **3**. In both fragments, the lithium atoms are located above and below the plane of the diimine fragment at equal distances from the nitrogen atoms. This arrangement of the lithium atoms differs from that of

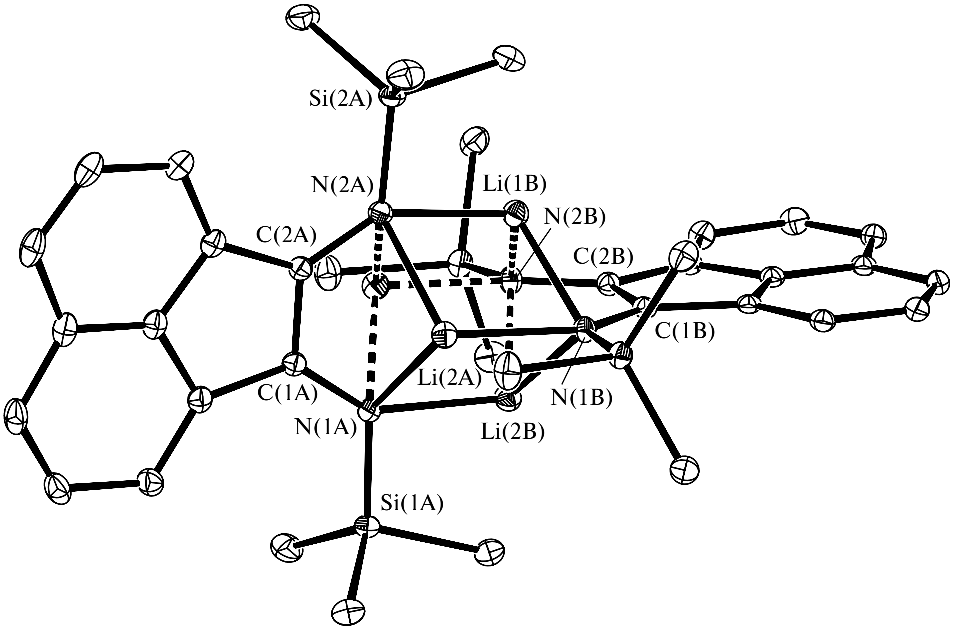


Fig. 5. Molecular structure of $[(\text{tms-BIAN})Li_2]_2$ (**3**). The hydrogen atoms are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

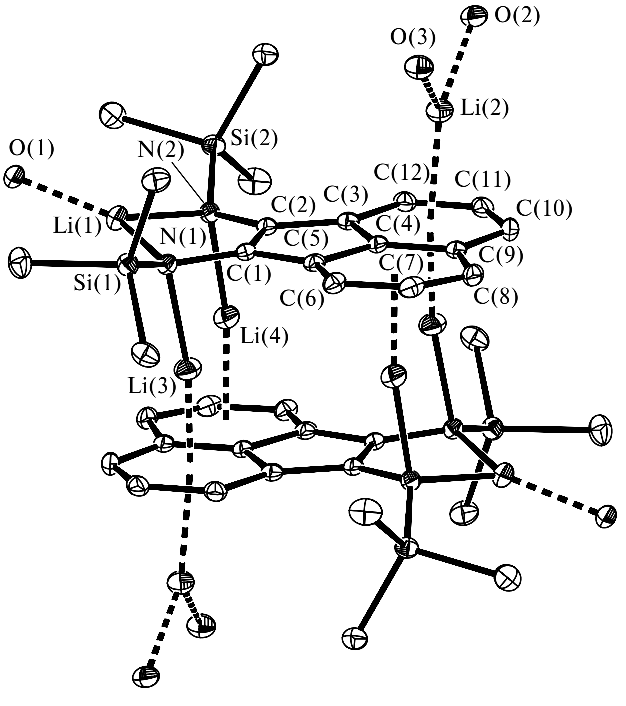


Fig. 6. Molecular structure of $[(\text{tms-BIAN})Li_4(Et_2O)_3]_2$ (**5**). The hydrogen atoms and the carbon atoms of the diethyl ether molecules are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

the sodium atoms in the monomeric structure of $(\text{dpp-BIAN})Na_2(Et_2O)_3$.[11a] In the latter compound, one of the sodium atom lies in the plane of the diimine moiety, whereas another sodium atom is located above the plane of the metallocycle Na—N(1)—C(1)—C(2)—N(2). Reduction of diimine **1** to the dianion is accompanied by a substantial change in the bond lengths in the diimine fragment. In the structure of **3**, the C—N bonds (1.4146(16) and 1.4141(16) Å) are longer than the corresponding bonds in **1**, whereas the C(1)—C(2) bond (1.4076(16) Å) is, on the contrary, shorter. The distinguishing structural feature of compound **3** is the unusually high coordination number of the nitrogen atoms (5). Each nitrogen atom is bound to one carbon atom, one silicon atom, and three lithium atoms. The Li—N distances have similar values (for example, N(1A)—Li(1A), 2.073(2) Å; N(1A)—Li(2A), 2.047(3) Å; N(1A)—Li(2B), 2.086(2) Å). The electron density on the nitrogen atoms in molecule **3** is conjugated with the unoccupied orbitals of the Me_3Si group (d orbitals of the Si atom and the antibonding orbitals of the Si—C bonds), which leads to an increase in the π character of the N—Si bond. This is evidenced by a shortening of these bonds in the structure of **3** (N(1A)—Si(1A), 1.7133(10) Å; N(2A)—Si(2A), 1.7161(10) Å) compared to those in **1** (N(1A)—Si(1A), 1.7446(12) Å; N(2A)—Si(2A), 1.7494(12) Å) and the upfield shift of the protons of the Me_3Si group in the ^1H NMR spectrum of compound **3** (see Table 1).

In the crystalline state, compound **5** exists as a coplanar centrosymmetric sandwich composed of two parallel tetraanions of tms-BIAN arranged in a head-to-tail fashion, four lithium atoms located between the planes of the sandwich, and four lithium atoms at the periphery of the sandwich (see Fig. 6). There are three types of lithium cations in molecule **5**. These cations differ in the charac-

Table 2. Crystallographic parameters, details of X-ray diffraction data collection, and characteristics of the structure refinement of compounds **1**, **3**, and **5**

Parameter	**1**	**3**	**5**
Molecular formula	$C_{18}H_{24}N_2Si_2$	$C_{18}H_{24}Li_2N_2Si_2$	$C_{60}H_{108}Li_8N_4O_6Si_4$
M	324.57	338.45	1149.38
Crystal system	Tetragonal	Triclinic	Monoclinic
Temperature/K	100	100	100
Space group	$P4(1)$	$P\bar{1}$	$P2(1)/n$
a/Å	11.5422(3)	10.8623(6)	11.6989(5)
b/Å	11.5422(3)	13.0096(8)	21.2204(10)
c/Å	13.8942(8)	15.1283(9)	14.9732(7)
α/deg	90	97.6560(10)	90
β/deg	90	110.4750(10)	112.6710(10)
γ/deg	90	98.2570(10)	90
V/Å^3	1851.02(13)	1942.8(2)	3430.0(3)
Z	4	4	2
d/g cm^{-3}	1.165	1.157	1.113
μ/mm^{-1}	0.190	0.182	0.133
F(000)	696	720	1248
Crystal dimensions/mm	0.40×0.30×0.25	0.38×0.25×0.08	0.24×0.23×0.17
Scan range, θ/deg	1.76—25.00	1.95—25.00	1.76—24.50
Indices of measured reflections	$-12 \le h \le 13$	$-12 \le h \le 12$	$-13 \le h \le 13$
	$-13 \le k \le 13$	$-15 \le k \le 9$	$-24 \le k \le 24$
	$-12 \le l \le 16$	$-17 \le l \le 17$	$-17 \le l \le 17$
Number of observed reflections	10211	10688	25516
Number of independent reflections	2872	6789	5708
R_{int}	0.0152	0.0155	0.0409
Absorption correction, max/min	0.9539/0.9277	0.9856/0.9339	0.9777/0.9687
Goodness-of-fit on F^2	1.075	1.055	1.027
R_1/wR_2 ($I > 2\sigma(I)$)	0.0229/0.0630	0.0367/0.0961	0.0401/0.0945
R_1/wR_2 (based on all reflections)	0.0231/0.0632	0.0426/0.0992	0.0553/0.1000
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.197/–0.165	0.391/–0.154	0.364/–0.150

Table 3. Selected bond lengths (d) and bond angles (ω) in the structure of **1**

Bond	d/Å	Angle	ω/deg
Si(1)—N(1)	1.7446(12)	N(1)—C(1)—C(2)	120.90(12)
Si(2)—N(2)	1.7494(12)	C(1)—N(1)—Si(1)	133.79(10)
N(1)—C(1)	1.2702(19)	N(2)—C(2)—C(1)	127.94(13)
N(2)—C(2)	1.2637(19)	C(2)—N(2)—Si(2)	132.74(11)
C(1)—C(2)	1.5478(18)	N(2)—C(2)—C(3)	126.42(13)
(C—C)$_{av}$ ($C_{10}H_8$)	1.399	N(1)—C(1)—C(5)	132.98(12)

ter of interaction with the tetraanion of tms-BIAN. The Li(1) atom slightly deviates from the plane of the diimine fragment and is bound to both nitrogen atoms, N(1) and N(2), and the O(1) atom of the diethyl ether molecule. The Li(2) atom is coordinated by two diethyl ether molecules, but is located at the outer side of the sandwich above one of the six-membered rings of the naphthalene moiety of the tms-BIAN ligand. Two other lithium atoms, Li(3) and Li(4) (and the symmetrically equivalent atoms), are located inside the sandwich, each atom being coordinated by one nitrogen atom and one six-membered ring of the second tetraanion of tms-BIAN. Earlier, we have observed[11a] an analogous dimeric structure of the tetraanion in the compound prepared by reduction of dpp-BIAN with sodium in THF. The dimeric structure containing four Li atoms between two layers of the tetraanions of corannulene has been established[26] by ^{7}Li NMR spectroscopy. Recently, we have observed[27] aggregation of lithium cations and the anionic π system of arene in the product $[C_{12}H_8]_2[@Li]_2[Li(Et_2O)_2]_2$ prepared by reduction of acenaphthylene with lithium in diethyl ether. In this derivative, two lithium atoms are located between two parallel dianions of acenaphthylene, and each Li atom is coordinated by the five- and six-membered rings of acenaphthylene. The polyanions of aromatic hydrocarbons have been extensively studied in recent years, because their physicochemical properties differ substantially from those of the neutral molecules. Recently,[28] tetra[1,2]benzenetetrabenzo[*a*,*e*,*i*,*m*]cyclohexadecene and hexa(4-*n*-dodecylbiphenyl)benzene have been reduced with lithium to the tetraanion and the hexaanion, respectively.[29]

Table 4. Selected bond lengths (*d*) and bond angles (ω) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Si(1A)—N(1A)	1.7133(10)	C(1A)—C(2A)	1.4076(16)	N(2A)—Li(1A)	2.051(3)
Si(2A)—N(2A)	1.7161(10)	N(1A)—Li(1A)	2.073(2)	N(2A)—Li(2A)	2.050(2)
N(1A)—C(1A)	1.4146(16)	N(1A)—Li(2A)	2.047(3)	N(2A)—Li(1B)	2.101(3)
N(2A)—C(2A)	1.4141(16)	N(1A)—Li(2B)	2.086(2)	$(C—C)_{av}$ $(C_{10}H_8)$	1.399
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(1A)—N(1A)—Si(1A)	125.81(9)	Si(1A)—N(1A)—Li(2B)	89.53(7)	C(2A)—N(2A)—Li(1A)	79.39(9)
Si(1A)—N(1A)—Li(2A)	135.26(8)	C(2A)—N(2A)—Si(2A)	125.88(9)	Si(2A)—N(2A)—Li(1A)	138.34(9)
Si(1A)—N(1A)—Li(1A)	132.04(9)	C(2A)—N(2A)—Li(2A)	83.07(9)	C(2A)—N(2A)—Li(1B)	144.72(10)
C(1A)—N(1A)—Li(2B)	144.38(10)	Si(2A)—N(2A)—Li(2A)	128.68(9)	Si(2A)—N(2A)—Li(1B)	89.39(7)

Table 5. Selected bond lengths (*d*) and bond angles (ω) in the structure of **5**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Si(1)—N(1)	1.6921(10)	Li(3)—C(9)$^{\#1}$	2.526(2)	Li(2)—C(10)	2.394(3)
O(1)—Li(1)	1.934(2)	Li(3)—C(10)$^{\#1}$	2.381(3)	Li(2)—C(11)	2.297(2)
O(3)—Li(2)	1.992(2)	Li(3)—C(11)$^{\#1}$	2.213(3)	Li(2)—C(12)	2.403(2)
N(1)—C(1)	1.4274(14)	Li(3)—C(12)$^{\#1}$	2.240(3)	Li(4)—C(4)$^{\#1}$	2.515(3)
N(1)—Li(1)	1.947(2)	Li(3)—Li(4)	3.015(3)	Li(4)—C(5)$^{\#1}$	2.402(3)
N(2)—Li(1)	1.966(2)	Si(2)—N(2)	1.6926(11)	Li(4)—C(6)$^{\#1}$	2.271(2)
Li(2)—C(3)	2.576(3)	O(2)—Li(2)	1.991(3)	Li(4)—C(7)$^{\#1}$	2.224(2)
Li(2)—C(4)	2.624(3)	C(1)—C(2)	1.4430(17)	Li(4)—C(8)$^{\#1}$	2.320(3)
Li(2)—C(9)	2.606(3)	N(2)—C(2)	1.4303(15)	Li(4)—C(9)$^{\#1}$	2.534(3)
Li(3)—C(3)$^{\#1}$	2.363(2)	N(1)—Li(3)	1.938(2)	$(C—C)_{av}$ $(C_{10}H_8)$	1.425
Li(3)—C(4)$^{\#1}$	2.457(2)	N(2)—Li(4)	1.963(2)		
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Si(1)—N(1)—Li(3)	110.36(9)	N(1)—Li(1)—N(2)	96.70(10)	Si(2)—N(2)—Li(1)	118.98(9)
Si(1)—N(1)—Li(1)	123.35(8)	Si(2)—N(2)—Li(4)	111.70(8)	O(2)—Li(2)—O(3)	100.62(11)

Note. #1 are the coordinates of the atoms generated by the symmetry operation.

The N—C distances in the diimine fragment of molecule **5** (1.4274(14) and 1.4303(15) Å) are slightly longer compared to those in the structure of **3**. Contrary to expectations, the C(1)—C(2) bond in the tetraanion is also longer than that in the dianion (**3**, 1.4076(16) Å; **5**, 1.4430(17) Å). Two-electron reduction of the naphthalene moiety leads to an expansion of the latter. Thus, the average C—C bond length in the rings (1.425 Å) in molecule **5** is larger than those in **1** and **3** (in both molecules, 1.399 Å). In molecule **5**, the coordination number of all nitrogen atoms is four. All Li—N bond lengths (N(1)—Li(1), 1.947(2) Å; N(2)—Li(1), 1.966(2) Å; N(1)—Li(3), 1.938(2) Å; N(2)—Li(4), 1.963(2) Å) in molecule **5** are substantially shorter than those in molecule **3**, which fact can be attributed to the smaller coordination number of the nitrogen atoms in molecule **5**. The Si—N bonds in molecule **5** (1.6921(10) and 1.6926(11) Å) are shorter than those in **3**. This indicates that molecule **5** has a common conjugated π system, which includes both the π orbitals of the six-membered rings and the orbitals of the nitrogen atoms. The common π system in molecule **5** is formed due to π-bonding between the carbon atoms (C(1)—C(5), 1.4208(17) Å; C(2)—C(3), 1.4158(16) Å). The corresponding interatomic distances in the structures of **1** and **3** are similar to the single C—C bond length (**1**: C(1)—C(5), 1.4899(19) Å; C(2)—C(3), 1.4834(19) Å; **3**: C(1)—C(5), 1.4850(18) Å; C(2)—C(3), 1.4831(18) Å).

To summarize, new acenaphthene-1,2-diimine containing the Me_3Si substituents at the nitrogen atoms can be successively reduced to the mono-, di-, tri-, and tetraanions. As expected, the mono- and trianions are paramagnetic, whereas the di- and tetraanions are diamagnetic. This ligand can be used to prepare transition and main-group metal complexes. The use of tms-BIAN as a neutral ligand in transition metal complexes instead of the Ar-BIAN ligands can substantially influence the reactivity of metal complexes because the π-acceptor properties of tms-BIAN are enhanced due to the n—d conjugation along the N—Si bond. This bond by itself is reactive toward nucleophilic reagents, for example, toward halogen derivatives. This property can be used for the synthesis of new acenaphthene-1,2-diimines containing various substituents at the nitrogen atoms, which cannot be derived from acenaphthenequinone. For example, this allows one to synthesize bis-alkyl derivatives and derivatives containing heteroorganic substituents.

Experimental

Since compounds **1—5** are sensitive to atmospheric oxygen and moisture, all operations associated with the synthesis, isolation, and identification were carried out *in vacuo* using the Schlenk technique. Acenaphthenequinone was purchased from Aldrich. Lithium bis(trimethylsilylamide) was synthesized by the reaction of Bu^nLi with $(Me_3Si)_2NH$ in hexane. Diethyl ether, THF, hexane, and toluene were dried with sodium benzophenone ketyl and withdrawn by vacuum condensation immediately before use. The IR spectra of suspensions of compounds **1**, **3**, and **5** were recorded on a FSM-1201 Fourier-transform spectrometer (Monitoring Ltd.) in Nujol mulls. The NMR spectra were measured at 20 °C on Bruker DPX 200 and Bruker DRX 400 instruments. The ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer.

1,2-Bis[(trimethylsilyl)imino]acenaphthene (1). Acenaphthenequinone (2.73 g, 15 mmol) was added to a solution of $(Me_3Si)_2NLi$ (5.0 g, 30 mmol) in toluene (100 mL). The reaction mixture was stirred at 50 °C for 60 min. Then Me_3SiCl (3.8 mL, 30 mmol) was added portionwise at ~20 °C. The resulting mixture was heated to 80 °C and stirred for 20 h. After cooling to ~20 °C, volatile products were removed *in vacuo*. Sublimation of the solid residue at 120 °C (10^{-2} Torr) afforded compound **1**. After recrystallization from hexane, compound **1** was isolated as orange needle-like crystals in a yield of 3.0 g (62%), m.p. 126 °C. Found (%): C, 66.58; H, 7.40. $C_{18}H_{24}N_2Si_2$ (324.57 g mol^{-1}). Calculated (%): C, 66.61; H, 7.45. IR, ν/cm^{-1}: 1926 w, 1869 w, 1811 w, 1673 s, 1598 w, 1303 w, 1249 s, 1151 w, 1107 w, 1050 w, 1006 m, 962 s, 905 m, 844 v.s, 788 w, 726 w, 692 m, 608 m, 544 w, 534 w, 460 m, 444 m, 426 w. ^1H NMR (400 MHz, $CDCl_3$), δ: 7.99 (d, 2 H, J = 8.3 Hz); 7.85 (d, 2 H, J = 7.1 Hz); 7.69 (dd, 2 H, J = 8.3 Hz, J = 7.1 Hz); 0.45 (s, 18 H, $SiMe_3$). ^1H NMR (200 MHz, THF-d_8), δ: 8.07 (d, 2 H, J = 8.3 Hz); 7.85 (d, 2 H, J = 7.1 Hz); 7.72 (dd, 2 H, J = 8.3 Hz, J = 7.1 Hz); 0.43 (s, 18 H, $SiMe_3$). ^{13}C NMR (50 MHz, THF-d_8), δ: 168.0, 143.5, 134.6, 132.2, 129.2, 128.6, 120.3, 1.1. ^{13}C NMR (100 MHz, C_6D_6), δ,: 167.4, 142.6, 133.8, 131.2, 128.3, 127.7, 119.6, 0.9. ^{29}Si NMR (39.7 MHz, THF-d_8), δ: −1.1. MS (101 °C), m/z (I_{rel} (%)): 73 $[SiMe_3]^+$ (98), 224 $[M - C_4H_9NSi]^+$ (75), 251 $[M - SiMe_3]^+$ (70), 309 $[M - Me]^+$ (29), 324 $[M]^+$ (100).

Dilithium 1,2-bis[(trimethylsilyl)imino]acenaphthene (3). A mixture of lithium metal (0.4 g, 57.2 mg-at.) and compound **1** (0.32 g, 1.0 mmol) in toluene (25 mL) was stirred using a magnetic stirrer at ~20 °C for 4 h. The resulting dark-blue solution was decanted from an excess of lithium. After removal of the toluene *in vacuo*, the residue was dissolved in hexane (30 mL) with heating. Crystallization from hexane afforded compound **3** in a yield of 0.18 g (53%) as dark-red, virtually black, crystals, m.p. 130 °C. Found (%): C, 63.71; H, 7.12. $C_{18}H_{24}Li_2N_2Si_2$ (338.45 g mol^{-1}). Calculated (%): C, 63.88; H, 7.15. IR, ν/cm^{-1}: 1656 w, 1615 w, 1587 w, 1520 m, 1450 s, 1434 s, 1376 w, 1358 w, 1345 w, 1291 v.s, 1248 s, 1190 w, 1143 m, 1127 m, 1095 s, 1015 m, 955 v.s, 910 w, 842 v.s, 771 s, 733 m, 678 w, 629 w, 615 w, 587 m, 550 w, 463 w. ^1H NMR (200 MHz, THF-d_8), δ: 7.03 (d, 2 H, J = 6.4 Hz); 6.92 (dd, 2 H, J = 8.2 Hz, J = 6.4 Hz); 6.82 (d, 2 H, J = 8.2 Hz); 0.17 (s, 18 H, $SiMe_3$).

Tetralithium 1,2-bis[(trimethylsilyl)imino]acenaphthene tris(diethyl etherate) (5). A mixture of lithium metal (0.4 g, 57.2 mg-at.) and compound **1** (0.32 g, 1.0 mmol) in Et_2O (30 mL) was vigorously stirred using a magnetic stirrer at 20 °C for 1 h. In the course of the reaction, the color of the solution gradually changed from orange to red, green, and finally brown-green. The resulting solution was decanted from an excess of lithium and concentrated by removal of the solvent *in vacuo*. Crystallization from Et_2O afforded compound **5** as dark-green, virtually black, crystals in a yield of 0.34 g (60%), m.p. > 200 °C. Found (%): C, 62.63; H, 9.32. $C_{30}H_{54}Li_4N_2O_3Si_2$ (574.69 g mol^{-1}). Calculated (%): C, 62.70; H, 9.47. IR, ν/cm^{-1}: 1553 w, 1502 w, 1450 s, 1413 w, 1380 v.s, 1360 v.s, 1292 m, 1249 m, 1232 s, 1161 s, 1069 s, 1075 s, 1036 s, 995 w, 964 s, 928 m, 845 s, 819 v.s, 788 m, 745 s, 699 s, 666 w, 656 w, 584 s, 540 m, 503 w, 431 w. ^1H NMR (200 MHz, THF-d_8), δ: 4.71 (d, 2 H, J = 8.2 Hz); 4.63 (dd, 2 H, J = 8.2 Hz, J = 5.8 Hz); 3.39 (q, 12 H, Et_2O, J = 7.0 Hz); 2.91 (d, 2 H, J = 5.8 Hz); 1.12 (t, 18 H, Et_2O, J = 7.0 Hz); −0.09 (s, 18 H, $SiMe_3$). ^{13}C NMR (50.3 MHz, THF-d_8), δ: 146.1, 132.6, 123.0, 120.0, 105.2, 96.6, 73.8, 65.3 (Et_2O), 14.7 (Et_2O), 4.1 ($SiMe_3$). ^{29}Si NMR (39.7 MHz, THF-d_8), δ: −16.1. ^7Li NMR (77.7 MHz, THF-d_8), δ: 3.35.

X-ray diffraction study of compounds 1, 3, and 5. X-ray diffraction data sets were collected on a Bruker AXS SMART APEX instrument (ω—φ-scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 100 K. Absorption corrections were applied using the SADABS program.[30] The structures were solved by direct methods using the SHELXS97 program package[31] and refined by the full-matrix least-squares method against F^2 with the use of the SHELXL97 program package.[32] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms in the structures of **1**, **3**, and **5** were located in difference electron density maps and refined isotropically. The geometric parameters of the structures were analyzed using the PLATON program.[33] The atomic coordinates were deposited with the Cambridge Structural Database.

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