2744 *Russian Chemical Bulletin, International Edition, Vol. 53, No. 12, pp. 2744—2750, December, 2004*

# Protonation of magnesium and sodium complexes containing dianionic diimine ligands. Molecular structures of 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene (dpp-BIAN), [(dph-BIAN)$H_2(Et_2O)$], and [(dpp-BIAN)HNa($Et_2O$)]

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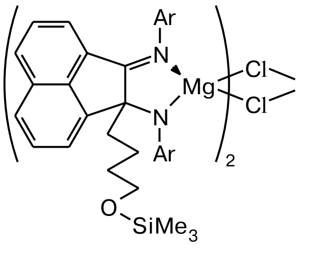
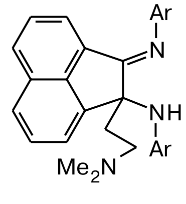
Hydrolysis of magnesium complexes containing the dianionic acenaphthenediimine ligands, (dpp-BIAN)Mg$(thf)_3$ (**1**), (dph-BIAN)Mg$(thf)_3$ (**2**), and (dtb-BIAN)Mg$(thf)_2$ (**3**) (dpp-BIAN is 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene; dph-BIAN is 1,2-bis{(2-diphenyl)imino}acenaphthene; dtb-BIAN is 1,2-bis{(2,5-di-*tert*-butylphenyl)imino}acenaphthene), affords the corresponding diamines (dpp-BIAN)$H_2$ (**4**), (dph-BIAN)$H_2(Et_2O)$ (**5**), and (dtb-BIAN)$H_2$ (**6**). Compounds **4** and **5** were isolated in the crystalline state and characterized by UV—Vis, IR, and $^1$H NMR spectroscopy. Partial hydrolysis of (dpp-BIAN)$Na_2(Et_2O)_3$ gave the crystalline (dpp-BIAN)HNa$(Et_2O)_2$ complex (**7**), which was also characterized by spectroscopic methods. The structures of compounds **5** and **7** and free diimine dpp-BIAN were established by X-ray diffraction analysis.

**Key words:** magnesium, sodium, diimine ligands, dianion, protonation, acenaphthylene-1,2-diamine.

Recently,[1,2] we have synthesized alkali and alkaline-earth metal complexes with various reduced forms of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN). In solvating solvents, alkali metals (Li, Na) successively reduce dpp-BIAN to the mono-, di-, tri-, and tetraanions $M^+_n$(dpp-BIAN)$^{n-}$ (M = Li, Na; $n$ = 1, 2, 3, or 4). Reduction of dpp-BIAN with metallic magnesium or calcium in THF affords exclusively complexes with the dpp-BIAN dianion of composition (dpp-BIAN)$^{2-}$M$^{2+}$(thf)$_n$ (M = Mg, $n$ = 3; M = Ca, $n$ = 4).[3] We have also synthesized[4] two new ligands of this type, *viz.*, 1,2-bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthene (dtb-BIAN) and 1,2-bis[(2-diphenyl)imino]acenaphthene (dph-BIAN), as well as their magnesium and calcium derivatives (dtb-BIAN)$^{2-}$Mg$^{2+}$(thf)$_2$ and (dph-BIAN)$^{2-}$M$^{2+}$L$_n$ (M = Mg, L = DME, $n$ = 2; M = Ca, L = thf, $n$ = 3).

Investigation of the reactions of the (dpp-BIAN)Mg$(thf)_3$ complex (**1**) with a series of organic compounds revealed their specific reactivity. For example, compound **1** reduces diphenyl ketone, resulting in oxidation of the dpp-BIAN dication to the radical anion and the formation of pinacolate [(dpp-BIAN)Mg(thf)]$_2$[μ-$O_2C_2Ph_4$], whereas the reaction of **1** with 9(10*H*)-anthracenone is accompanied by deprotonation of the phenol tautomer to form the anthryl-9-oxy derivative (dpp-BIAN)Mg($OC_{14}H_9$)(thf)$_2$.[5] The reactions of complex **1** with halogen-containing inorganic (CuCl, $SiCl_4$, $I_2$) and organic ($Ph_3SnCl$, 1,2-dibromo-1,2-diphenylethane) compounds also lead to oxidation of the dpp-BIAN dianion to the radical anion and the formation of the unsymmetrical [(dpp-BIAN)Mg(μ-X)(thf)]$_2$ (X = Cl, Br) and (dpp-BIAN)MgI(DME) complexes.[6] The reactions of complex **1** with $Me_3SiCl$ and $Me_2NCH_2CH_2Cl$ re-





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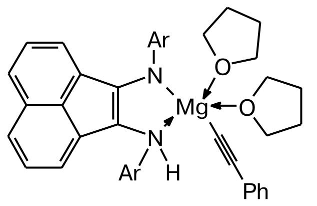
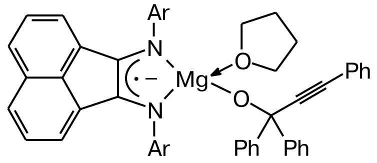
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2634—2640, December, 2004.

sulted in the addition of the alkyl group to the imine carbon atom of the ligand, which has not been observed earlier for diimine derivatives of main-group metals. The reaction with $Me_3SiCl$ is accompanied by the THF ring opening.

The reactions of complex **1** with various C—H-, N—H-, and O—H-acids proceed in an unusual fashion. Unlike 9(10*H*)-anthracenone, these compounds are not deprotonated with complex **1**; instead, they are bound to this complex. For example, the reaction of complex **1** with phenylacetylene affords the phenylethynyl derivative [dpp-BIAN(H)]Mg(C≡CPh)$(thf)_2$. However, the latter eliminates the hydrogen atom upon the insertion of diphenyl ketone, which is accompanied by oxidation of the dpp-BIAN ligand to the radical anion and the formation of alkoxide (dpp-BIAN)Mg[OC$(Ph_2)$C≡CPh](thf).[7]



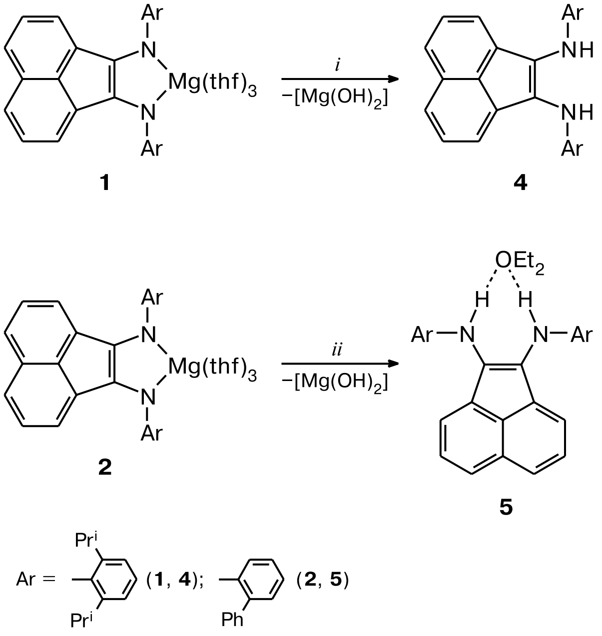


As part of our continuing studies on protonation of metal complexes containing the dianionic dpp-BIAN ligand, we investigated hydrolysis of sodium and magnesium derivatives. Hydrolysis of magnesium complexes was found to produce the corresponding acenaphthylene-1,2-(*N,N′*-aryl)diamines regardless of the amount of $H_2O$ used in the reaction, whereas the reaction of the sodium complex with an equimolar amount of $H_2O$ resulted in protonation of only one nitrogen atom.

## Results and Discussion

**Hydrolysis of magnesium acenaphthenediimine complexes.** The starting solutions of the (dpp-BIAN)Mg$(thf)_3$ (**1**), (dph-BIAN)Mg$(thf)_n$ (**2**), and (dtb-BIAN)Mg$(thf)_2$ (**3**) complexes were prepared *in situ* by reducing the corresponding diimine (1 mmol) in THF with an excess of magnesium.[3,4] Since it was difficult to add a strictly stoichiometric amount of liquid water, hydrolysis was carried out using slow diffusion by delivering water vapor to a solution of the complex under vacuum. The completeness of the reaction was monitored by the change in the color of the solution of the complex. When exposed to water vapor, the solutions of complexes **1—3** turned violet-red. In the first two cases, acenaphthylene-1,2-(*N,N′*-aryl)diamines, *viz*., (dpp-BIAN)$H_2$ (**4**) and (dph-BIAN)$H_2(Et_2O)$ (**5**), respectively, were obtained after removal of the solvent and extraction of organic products with hexane and diethyl ether (Scheme 1).

**Scheme 1**



*i*. $H_2O$, 1) THF, 2) hexane; *ii*. $H_2O$, 1) THF, 2) $Et_2O$.

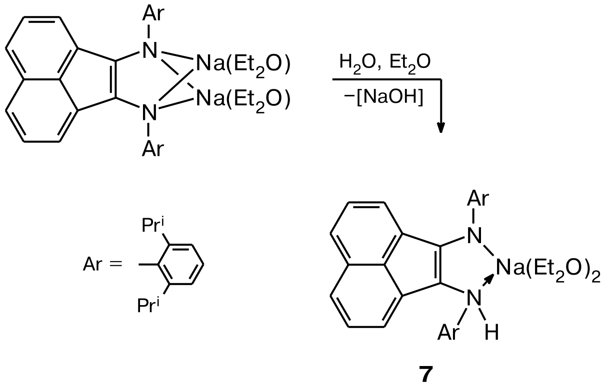
High solubility of diamine (dtb-BIAN)$H_2$ (**6**) that formed upon hydrolysis of complex **3** did not allow us to isolate it in the crystalline state. However, the $^1H$ NMR spectrum of the reaction mixture confirms the presence of compound **6**. The spectrum of a solution in THF-$d_8$ shows two singlets at δ 1.03 and 1.31 assigned to the protons of the Me groups of the *tert*-butyl substituents. The signal for the proton of the amino group appears as a singlet at δ 5.77.

Compounds **4** and **5** were crystallized from hexane and diethyl ether as dark-red needle-like and prismatic crystals, respectively. Unexpectedly, water-stable diamines **4** and **5** in solutions were virtually immediately oxidized with atmospheric oxygen to give the starting diimines. In the IR spectra of diamines **4** and **5**, the N—H stretching bands are observed at 3370 and 3350 $cm^{-1}$, respectively. As in dpp-BIAN, there is no free rotation of the Ph rings about the N—$C_{ipso}$ bond in compound **4** due to steric effects, which is reflected in the presence of two different signals for the Me protons of the $Pr^i$ substituents in the $^1H$ NMR spectrum (doublets at δ 1.26 and 1.19). Four equivalent methine protons of the $Pr^i$ groups are observed as a septet at δ 3.63. In the $^1H$ NMR spectrum of compound **5**, the signals for nine of twelve aromatic protons lie in a narrow region, which hinders their assignment. Three other signals are observed as a doublet of triplets and two triplets of doublets at δ 7.48, 7.06, and 6.87, respectively. In the $^1$H NMR spectra of compounds **4** and **5** (both in $C_6D_6$), the signals for the N—H protons appear as singlets at δ 5.08 and 5.65, respectively. Compared to the starting diimines, compounds **4** and **5** are more brightly colored. Presumably, their electronic structures are similar to metal complexes, such as (dpp-BIAN)$Na_2(Et_2O)_3$ [1,2] and (dpp-BIAN)Mg(thf)$_3$.[3] In the visible region of the spectrum of the (dpp-BIAN)$Na_2(Et_2O)_3$ complex, the absorption band has a maximum at 640 nm,[2] whereas the spectra of compounds **4** and **5** in $Et_2O$ show bands with maxima at 536 and 500 nm, respectively. In a THF solution, the maximum of the absorption band of compound **4** is observed at 550 nm. In THF and $Et_2O$ solutions, compound **4**, apparently, forms complexes with these ethers through N—H...$O_{solv}$ hydrogen bonds (solv is the solvent).

Protonation of the magnesium derivatives with water differs from their protonation with C—H-, N—H-, and O—H-acids. For example, the reaction of (dpp-BIAN)Mg(thf)$_3$ with even a fivefold excess of phenylacetylene is not accompanied by protonation of the second nitrogen atom and gives the phenylethynyl derivative [dpp-BIAN(H)]Mg(C≡CPh)(thf)$_2$ as the final product.[7]

**Hydrolysis of (dpp-BIAN)$Na_2(Et_2O)_3$.** Hydrolysis of the (dpp-BIAN)$Na_2(Et_2O)_3$ compound, which was prepared *in situ* by reducing dpp-BIAN with two equivalents of sodium in diethyl ether, with an excess of water afforded diamine **4**. However, slow diffusion of water vapor into a solution of the sodium complex initially led to a change in the color of the solution to dark-blue, and only further addition of $H_2O$ resulted in the violet-red color of the solution. The dark-blue ethereal solution was concentrated to give the (dpp-BIAN)HNa$(Et_2O)_2$ compound (**7**) as dark-blue crystals sensitive to atmospheric oxygen and moisture (Scheme 2).

**Scheme 2**



Compound **7** is an intermediate in the transformation of (dpp-BIAN)$Na_2(Et_2O)_3$ into diamine **4**. In the IR spectrum of complex **7**, a pronounced N—H stretching band is absent. In the $^1$H NMR spectra of compound **7** both in THF-$d_8$ and $C_6D_6$, all signals are strongly broadened, which, in our opinion, indicates that dynamic processes occur in solution. Slow (on the NMR time scale) proton migration between two nitrogen atoms can be one of such processes. We have observed an analogous spectral pattern for [dpp-BIAN(H)]Mg(C≡CPh)(thf)$_2$.[7]

In the $^1$H NMR spectrum of compound **7** in $C_6D_6$, the Me protons of the Pr$^i$ substituents appear as one broad signal at δ 1.2, and the signals for the methine protons of these substituents are observed as broad signals at δ 3.85 and 3.45. The signals for the aromatic protons are also strongly broadened and are observed at δ 7.5—6.0. Although the spectrum is poorly informative, it has a broad signal for the proton of the amino group at δ 4.98. In the spectrum in THF-$d_8$, the corresponding signal has virtually the same chemical shift (δ 5.05). The absorption band in the UV—Vis absorption spectrum with a maximum at 625 nm corresponds to the blue color of complex **7** in a diethyl ether solution.

**Molecular structures of compounds 5, 7, and dpp-BIAN.** In spite of the fact that dpp-BIAN is widely used in transition metal chemistry,[8—12] the molecular structure of the free ligand has not been determined earlier. Crystals of dpp-BIAN suitable for X-ray diffraction analysis were grown from toluene. The structures of compounds **5**, **7**, and dpp-BIAN were established by X-ray diffraction analysis and are shown in Figs 1, 2, and 3, respectively. The crystallographic data, details of X-ray data collection, and characteristics of structure refinement are given in Table 1. Selected bond lengths and bond angles for the structures of **5**, **7**, and dpp-BIAN are listed in Table 2.

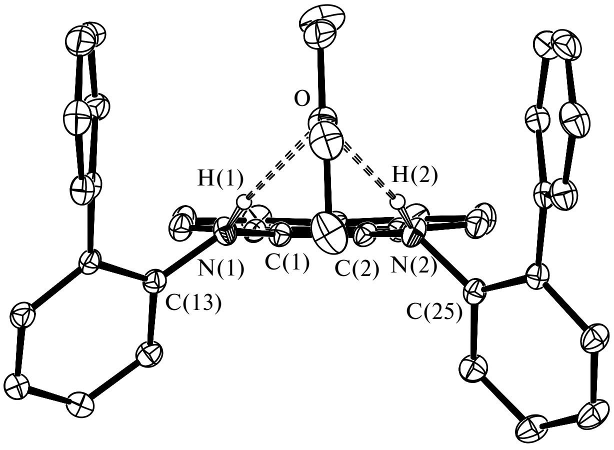


**Fig. 1.** Molecular structure of (dph-BIAN)$H_2(Et_2O)$ (**5**) with displacement ellipsoids drawn at the 30% probability level. The H atoms, except for those bound to the N atoms, are omitted.

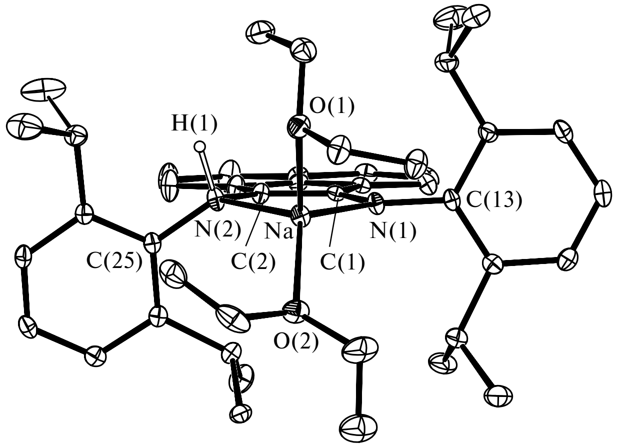


**Fig. 2.** Molecular structure of (dpp-BIAN)HNa($Et_2O$)$_2$ (**7**) with displacement ellipsoids drawn at the 30% probability level. The H atoms, except for H(1), are omitted.

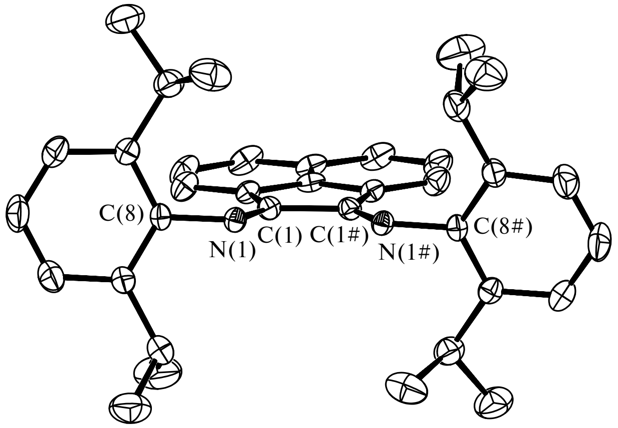


**Fig. 3.** Molecular structure of dpp-BIAN with displacement ellipsoids drawn at the 30% probability level. The H atoms are omitted.

It should be noted that the crystal structure of diamine **5** (see Fig. 1) contains the diethyl ether molecule coordinated to the H(1) and H(2) atoms of **5** through hydrogen bonds. These H atoms were localized from difference Fourier syntheses at the N(1) and N(2) atoms at distances of 0.92(3) [N(1)] and 0.86(3) [N(2)] Å, respectively. The H(1)—O and H(2)—O distances are 2.206(3) and 2.134(3) Å, respectively. The sums of the bond angles at

**Table 1.** Crystallographic data, characteristics of X-ray data collection, and details of structure refinement for compounds **5**, **7**, and dpp-BIAN

| Parameter | **5** | **7** | dpp-BIAN |
|---|---|---|---|
| Molecular formula | $C_{40}H_{36}N_2O$ | $C_{44}H_{61}N_2NaO_2$ | $C_{36}H_{40}N_2$ |
| Molecular weight | 560.71 | 672.94 | 500.70 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Temperature/K | 173 | 100 | 173 |
| Space group | $P2_1/c$ | $P\bar{1}$ | $C2/c$ |
| $a$/Å | 11.2028(1) | 10.5184(17) | 15.4976(7) |
| $b$/Å | 15.2839(1) | 13.792(2) | 8.8279(4) |
| $c$/Å | 18.5180(1) | 14.580(2) | 21.5282(11) |
| $\alpha$/deg | 90 | 79.307(3) | 90 |
| $\beta$/deg | 101.598(1) | 70.938(3) | 93.88 |
| $\gamma$/deg | 90 | 89.168(3) | 90 |
| $V$/Å$^3$ | 3105.96(4) | 1962.0(6) | 2938.6(2) |
| $Z$ | 4 | 2 | 4 |
| $d$/g cm$^{-3}$ | 1.199 | 1.139 | 1.132 |
| $\mu$/mm$^{-1}$ | 0.071 | 0.078 | 0.065 |
| $F$(000) | 1192 | 732 | 1080 |
| Crystal dimensions/mm | 0.36×0.32×0.16 | 0.40×0.40×0.10 | 0.52×0.31×0.18 |
| Scan range, θ/deg | 1.74—26.00 | 1.50—25.00 | 1.90—25.00 |
| Ranges of $h, k, l$ indices | $-13 \le h \le 12$ | $-12 \le h \le 12$ | $-18 \le h \le 18$ |
|  | $-18 \le k \le 18$ | $-16 \le k \le 16$ | $-6 \le k \le 10$ |
|  | $-22 \le l \le 19$ | $-17 \le l \le 17$ | $-25 \le l \le 25$ |
| Number of observed reflections | 19920 | 15188 | 8543 |
| Number of independent reflections | 6052 | 6866 | 2586 |
| $R_{int}$ | 0.0847 | 0.0192 | 0.0815 |
| Goodness-of-fit on $F^2$ | 1.002 | 1.057 | 1.050 |
| $R_1/wR_2$ ($I > 2\sigma(I)$) | 0.0612/0.1127 | 0.0692/0.1853 | 0.0759/0.1843 |
| $R_1/wR_2$ (based on all parameters) | 0.1207/0.1317 | 0.0833/0.1945 | 0.1334/0.2134 |
| Residual electron density/e Å$^{-3}$, $\rho_{max}/\rho_{min}$ | 0.244/–0.288 | 0.944/–0.329 | 0.362/–0.263 |

**Table 2.** Selected bond lengths (*d*) and bond angles (ω) in molecules **5**, **7**, and dpp-BIAN

| Parameter | **5** | **7** | dpp-BIAN |
|---|---|---|---|
| Bond | | *d*/Å | |
| Na—N(1) | — | 2.3385(17) | — |
| Na—N(2) | — | 2.4429(17) | — |
| H(1)—N(2) | 0.92(3) | 1.04(3) | — |
| H(2)—N(2) | 0.86(3) | — | — |
| Na—O(1) | — | 2.3694(15) | — |
| Na—O(2) | — | 2.3080(15) | — |
| H(1)—O | 2.206(3) | — | — |
| H(2)—O | 2.134(3) | — | — |
| C(1)—N(1) | 1.395(3) | 1.347(2) | — |
| C(2)—N(2) | 1.400(3) | 1.434(2) | — |
| C(1)—C(2) | 1.369(3) | 1.395(3) | — |
| C(13)—N(1) | 1.400(3) | 1.403(2) | — |
| C(25)—N(2) | 1.394(3) | 1.433(2) | — |
| C(1)—N(1) | — | — | 1.282(4) |
| C(1#)—N(1#) | — | — | 1.282(4) |
| C(1)—C(1#) | — | — | 1.534(6) |
| C(2)—N(1) | — | — | 1.422(4) |
| C(2#)—N(1#) | — | — | 1.422(4) |
| Angle | | ω/deg | |
| C(1)—N(1)—C(13) | 122.85(19) | 120.18(14) | 122.9(2) |
| C(1)—N(1)—H(1) | 115.37(19) | — | — |
| C(13)—N(1)—H(1) | 120.46(19) | — | — |
| C(2)—N(2)—C(25) | 122.82(18) | 117.08(13) | 122.9(2) |
| C(2)—N(2)—H(2) | 117.72(19) | 106.97(13) | — |
| C(25)—N(2)—H(2) | 117.52(19) | — | — |
| N(1)—Na(1)—N(2) | — | 76.48(6) | — |
| O(1)—Na(1)—O(2) | — | 94.20(6) | — |
| C(1)—N(1)—Na(1) | — | 110.14(11) | — |
| C(13)—N(1)—Na(1) | — | 129.46(11) | — |
| C(2)—N(2)—Na(1) | — | 104.80(11) | — |
| C(25)—N(2)—Na(1) | — | 120.35(10) | — |

the nitrogen atoms [N(1), 358.7°; N(2), 358.1°] are only slightly smaller than the sum of the angles for the ideal trigonal-planar environment (360°), which indicates that the lone electron pairs of the N atoms are conjugated with the π-system of the Ph rings. As a result of conjugation, the H(1) and H(2) protons become more acidic, which is favorable for strong hydrogen bonding with the O atom of the ether molecule. Diamine **5** can exist as two isomers, which differ in the mutual arrangement of the *ortho*-substituents in the aniline fragments relative to the plane of acenaphthylene. Unlike the starting dph-BIAN compound (*E*,*Z*-*anti* isomer)[4] and related germylene (dph-BIAN)Ge (*E*,*E*-*anti* isomer),[13] diamine **5** is the *syn* isomer. An analogous geometry of the ligand has been observed[4] in the (dph-BIAN)Ca(thf)$_3$ complex. In the biphenyl groups bound to the N(1) and N(2) atoms, the Ph rings are twisted with respect to each other by 59.6 and 44.5°, respectively.

In complex **7** (see Fig. 2), the Na atom is bound to two N atoms of the chelating amido/amino ligand and lies virtually in the mean plane of the N(1)—C(1)—C(2)—N(2) fragment (C(1)—C(2)—N(2)—Na(1) torsion angle is 5.2°). The differences in the amido and amino functions of two N atoms are manifested in the different lengths of their bonds with the Na atom. The Na—N(1) amide bond [2.3385(17) Å] is shorter than the Na—N(2) coordination bond [2.4429(17) Å]. In the difference Fourier synthesis, the H(1) atom was revealed at a distance of 1.04(3) Å from the N(2) atom, which is larger than the N—H bond lengths in the structure of **5** [0.92(3) and 0.86(3) Å]. Hence, it can be suggested that the interaction between the H(1) and N(2) atoms in molecule **7** is more ionic than that in molecule **5**. This is confirmed by the absence of the N—H stretching band in the IR spectrum. Since the IR spectrum of compound **7** was recorded at room temperature, it was worthwhile establishing the structure of complex **7** and, primarily, determining the position of the H atom at room temperature. Due to abnormally high thermal motion of the Et$_2$O molecules, the quality of X-ray diffraction data at 293 K is noticeably lower than that at 100 K. However, it should be noted that the H atom at room temperature was localized at an even larger distance from the N(2) atom (1.22(8) Å). The sums of the bond angles at the N(1) (359.8°) and N(2) (342.2°) atoms (see Table 1) show that the N(1) atom has a trigonal-planar geometry, whereas the geometry of the environment about the N(2) atom is intermediate between the trigonal-planar and pyramidal (sum of the angles is 328.0°).

The dpp-BIAN molecule (see Fig. 3) is located on a crystallographic twofold rotation axis passing along the C—C bond between two six-membered rings of the naphthalene fragment. The C(1)—N(1) and C(1#)—N(1#) distances [1.282(4) Å] correspond to the carbon—nitrogen double bond, whereas the C(1)—C(1#) distance [1.534(6) Å] is nearly equal to the length of the C—C single bond.

The C—N distances in molecule **5** [1.395(3) and 1.400(3) Å] are longer than those in the free diimines dph-BIAN [4] and dpp-BIAN by ~0.13 Å and are close to the corresponding distances in the (dph-BIAN)Ca(thf)$_3$ [1.421(11) and 1.405(11) Å][4] and (dpp-BIAN)Na$_2$(Et$_2$O)$_3$ [1.387(4) and 1.386(4) Å][1] molecules. The C(1)—C(2) bond in compound **5** is, on the contrary, shortened compared to those in dph-BIAN [4] and dpp-BIAN [9] (its length is 1.369(3) Å). The asymmetry of the structure of complex **7** is manifested in the difference in the C—N bond lengths in the diimine fragment of the molecule. The C(1)—N(1) bond [1.347(2) Å] is substantially shorter than the C(2)—N(2) bond [1.434(2) Å], whose length is, in turn, similar to the corresponding bond lengths in molecule **5**. The C(1)—N(1) distance is comparable to the C—N bond lengths in the sodium complex [(dpp-BIAN)Na]$_2$ with the dpp-BIAN radical anion [N(1)—C(1), 1.3239(18) Å; N(2)—C(2), 1.3326(19) Å].[1] In all cases, reduction of the dpp-BIAN radical anion to the dianion leads to shortening of the C(1)—C(2) bond. For example, the C(1)—C(2) bond length in [(dpp-BIAN)Na]$_2$ is larger than that in (dpp-BIAN)Na$_2$(Et$_2$O)$_3$ (1.446(2) and 1.402(4) Å, respectively).[1] The C(1)—C(2) bond in compound **7**, like that in the BIAN dianion in the sodium complex, is short (1.395(3) Å).

To summarize, hydrolysis of the magnesium and sodium complexes containing the dianionic acenaphthenediimine ligands affords acenaphthylene-1,2-bis(*N*,*N*´-aryl)diamines. Spectroscopic and X-ray diffraction data and the fact that these diamines are readily oxidized with atmospheric oxygen suggest that they can formally be considered as compounds of the dianions of the corresponding BIAN ligands with two H$^+$ cations. The latter, unlike metal cations, do not form chelate rings, and are located at the N atoms. Isolation of the partially protonated (dpp-BIAN)HNa(Et$_2$O) complex (**7**) provides evidence that there is a continuum of various dianionic forms of the BIAN ligands. Diamines **4—6**, like metal complexes with the BIAN dianions, can be used as reducing agents in organic synthesis. Unlike metal complexes, these compounds can serve as sources of H$^•$ rather than as electron sources. Studies of the reactions of diamines **4—6** with organic compounds are presently underway.

## Experimental

Since all the above-mentioned compounds, except for diimines dpp-BIAN, dph-BIAN, and dtb-BIAN, are sensitive to atmospheric oxygen and moisture, operations associated with their synthesis, isolation, and identification were carried out *in vacuo* using the Schlenk technique. Diimine dpp-BIAN was prepared by condensation of acenaphthenequinone with the corresponding aniline (both were purchased from Aldrich) in acetonitrile.[14] Complexes **1—3** were synthesized according to procedures described earlier.[3,4] In all cases, solutions of complexes **1—3** in THF were prepared from the corresponding diimine (1.0 mmol) and an excess of magnesium metal and were used in hydrolysis *in situ*. Tetrahydrofuran, diethyl ether, and hexane were dried, stored over sodium benzophenone ketyl, and distilled immediately before use. The yields of the products are given with respect to the amount of diimine (1.0 mmol) used for the synthesis of complexes **1—3**. The IR spectra were recorded on a Specord M-80 spectrometer (Nujol mulls). The NMR spectra were measured on Bruker DPX 200 and Bruker ARX 400 spectrometers; the chemical shifts are given in the δ scale relative to the chemical shifts of the residual protons of deuterated solvents.

***N*,*N*´-Bis-(2,6-diisopropylphenyl)acenaphthylene-1,2-diamine (4).** Water vapor was slowly supplied to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in THF, with cooling (10—0 °C) until the solution turned violet-red. Volatile products were removed *in vacuo*, and the product was dissolved in hexane and crystallized to prepare compound **4** in a yield of 0.48 g (96%) as dark-red needle-like crystals, m.p. 143 °C. Found (%): C, 83.44; H, 7.72. $C_{36}H_{42}N_2$. Calculated (%): C, 86.01; H, 8.42; N, 5.57. Reliable elemental analysis data were not obtained because of high sensitivity of compound **4** to atmospheric oxygen and moisture. IR, ν/cm$^{-1}$: 3370 w, 1570 v.s, 1330 m, 1255 m, 1200 w, 1100 m, 1050 w, 1025 w, 915 m, 800 s, 770 s, 750 v.s, 720 s. $^1$H NMR (200 MHz, $C_6D_6$, 20 °C), δ: 7.36—7.20 (m, 8 H); 7.01 (t, 2 H, *J* = 8.0 Hz); 6.57 (d, 2 H, *J* = 7.0); 5.08 (s, 2 H, NH); 3.63 (sept, 4 H, *J* = 6.8 Hz); 1.26 and 1.19 (both d, 12 H each, *J* = 6.8 Hz).

***N*,*N*´-Bis-biphenyl-2-ylacenaphthylene-1,2-diamine (5).** Water vapor was slowly supplied to a solution of complex **2**, which was prepared from dph-BIAN (0.49 g, 1.0 mmol) in THF, with cooling (10—0 °C) until the solution turned dark-red. The solvent was removed *in vacuo*, and diethyl ether (50 mL) was added to the residue. The reaction product was extracted with diethyl ether until the solution ceased to turn red. Compound **5** was isolated by crystallization from Et$_2$O as dark-red prismatic crystals in a yield of 92% (0.51 g), m.p. 80 °C. Found (%): C, 85.42; H, 6.32. $C_{40}H_{36}N_2O$. Calculated (%): C, 85.68; H, 6.47. IR, ν/cm$^{-1}$: 3350 m, 3315 m, 1600 s, 1505 s, 1490 s, 1430 s, 1360 m, 1300 m, 1280 s, 1230 w, 1150 m, 1100 s, 1035 w, 1005 w, 930 w, 850 w, 820 w, 785 s, 740 v.s, 700 s, 610 w, 535 s. $^1$H NMR (200 MHz, $C_6D_6$, 20 °C), δ: 7.48 (dt, 2 H, *J* = 9.0 Hz, *J* = 3.5 Hz); 7.40—7.12 (m, 18 H); 7.06 (td, 2 H, *J* = 8.0 Hz, *J* = 1.5 Hz); 6.87 (td, 2 H, *J* = 7.2 Hz, *J* = 1.2 Hz); 5.65 (s, 2 H, NH); 3.36 (q, 4 H, CH$_2$O, *J* = 7.0 Hz); 1.20 (t, 6 H, $C\underline{H}_3CH_2O$, *J* = 7.0 Hz).

***N*,*N*´-Bis-(2,5-di-*tert*-butylphenyl)acenaphthylene-1,2-diamine (6).** Water vapor was slowly supplied to a solution of complex **3**, which was prepared from dtb-BIAN (0.56 g, 1.0 mmol) in THF, with cooling (10—0 °C) until the solution turned violet-red. The solvent was removed *in vacuo*, and diethyl ether (30 mL) was added to the residue. After centrifugation, the solution was decanted from the precipitate, and an aliquot of the solution (0.5 mL) was placed in an NMR tube. Volatile products were removed from the main solution *in vacuo*. Compound **6** was obtained as a dark-red oil in a yield of 0.55 g (98%). $^1$H NMR (200 MHz, THF-d$_8$, 20 °C), δ: 7.43 (d, 2 H, *J* = 8.3 Hz); 7.18 (t, 2 H, *J* = 6.8 Hz); 7.15 (d, 2 H, *J* = 2.0 Hz); 7.13 and 7.01 (both d, 2 H each, *J* = 6.8 Hz); 6.79 (dd, 2 H, *J* = 8.3 Hz, *J* = 2.0 Hz); 5.77 (s, 2 H); 1.31 and 1.03 (both s, 18 H each).

**Acenaphthylene-1-(2,6-diisopropylphenylamino)-2-(2,6-diisopropylphenylamido)sodium diethyl etherate (7).** Water vapor was slowly supplied to a solution of the (dpp-BIAN)Na$_2$(Et$_2$O)$_3$ complex, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) and sodium (0.046 g, 2.0 mmol) in Et$_2$O (35 mL), with cooling (10—0 °C) until the solution turned dark-blue. Then the solution was separated from insoluble products by centrifugation and decantation. Compound **7** was isolated from the concentrated solution (15 mL) as large dark-blue prismatic crystals in a yield of 0.37 g (92%), m.p. 192 °C. Found (%): C, 77.12; H, 8.75. $C_{44}H_{61}N_2NaO_2$. Calculated (%): C, 78.53; H, 9.14. Reliable elemental analysis data were not obtained because of high sensitivity of compound **7** to atmospheric oxygen and moisture. IR, ν/cm$^{-1}$: 1665 w, 1625 w, 1580 s, 1500 v.s, 1400 s, 1370 v.s, 1315 s, 1245 m, 1170 s, 1105 s, 1095 s, 1065 s, 905 m, 805 m, 880 s, 855 v.s, 845 v.s, 690 m. $^1$H NMR (200 MHz, $C_6D_6$, 20 °C), δ: 7.35, 7.15, 6.95, 6.55, 6.18, 4.98, 3.85, 3.45 ($C\underline{H}CH_3$); 3.18 ($Et_2O$); 1.20 ($CHC\underline{H}_3$); 0.92 ($Et_2O$).

**X-ray diffraction study of compounds 5, 7, and dpp-BIAN.** X-ray diffraction data for diamine **5** and dpp-BIAN were measured on a Siemens SMART CCD diffractometer (ω—φ scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. X-ray diffraction data for compound **7** were collected on a Bruker AXS SMART APEX diffractometer (ω—φ scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 100 K. The absorption corrections were applied using the SADABS program.[15] The structures were solved by direct methods using the SHELXS97 program package[16] and refined by the full-matrix least-squares method against $F^2$ using the SHELXL97 program package.[17] All non-hydrogen atoms were refined anisotropically. The H atoms bound to the N atoms were revealed from difference Fourier syntheses, and the other hydrogen atoms were placed in idealized positions ($U_{iso}$ = 0.08 Å$^2$). The atomic coordinates were deposited with the Cambridge Structural Database.

We thank Yu. A. Kurskii for recording NMR spectra and T. I. Lopatina for measuring UV—Vis spectra.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32246), the State Program for the Support of Leading Scientific Schools (Grant NSh-1652.2003.3), and the Foundation for Support of National Science.

## References

1. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 3294.
2. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, V. K. Cherkasov, G. K. Fukin, and M. A. Lopatin, *Eur. J. Inorg. Chem.*, 2004, **2**, 388.
3. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2003, **18**, 3336.
4. I. L. Fedushkin, V. A. Chudakova, A. A. Skatova, N. M. Khvoinova, Yu. A. Kurskii, T. A. Glukhova, G. K. Fukin, S. Dechert, M. Hummert, and H. Schumann, *Z. Anorg. Allg. Chem.*, 2004, **630**, 501.
5. I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Chem. — A Eur. J.*, 2003, **9**, 5778.
6. I. L. Fedushkin, A. A. Skatova, A. N. Lukoyanov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2004, No. 12 [*Russ. Chem. Bull., Int. Ed.*, 2004, No. 12].
7. I. L. Fedushkin, N. M. Khvoinova, A. A. Skatova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 5223.
8. M. W. van Laren and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1999, **38**, 3715.
9. R. van Belzen, H. Hoffmann, and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1997, **36**, 1743.
10. G. A. Grasa, R. Singh, E. D. Stevens, and S. P. Nolan, *J. Organomet. Chem.*, 2003, **687**, 269.
11. A. E. Cherian, E. B. Lobkovsky, and G. W. Coates, *Chem. Commun.*, 2003, **20**, 2566.
12. M. D. Leatherman, S. A. Svejda, L. K. Johnson, and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 3068.
13. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, N. M. Khvoinova, A. Yu. Baurin, S. Dechert, M. Hummert, and H. Schumann, *Organometallics*, 2004, **23**, 3714.
14. A. A. Paulovicova, U. El-Ayaan, K. Shibayama, T. Morita, and Y. Fukuda, *Eur. J. Inorg. Chem.*, 2001, 2641.
15. G. M. Sheldrick, *Empirical Absorption Correction Program*, Universität Göttingen, Göttingen (Germany), 1996.
16. G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, Göttingen (Germany), 1990.
17. G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen (Germany), 1997.

*Received May 19, 2004;*
*in revised form September 6, 2004*