# New Bromine-Containing Bis(arylimino)acenaphthenes and Related Metal Complexes

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**Abstract**—The condensation reactions of 5-bromoacenaphthenequinone with 2,6-diisopropylaniline and 4-bromo-2,6-di-*iso*-propylaniline afford new mono- and tribromosubstituted bis(arylimino)acenaphthenes: 1,2-bis[(2,6-diisopropylphenyl)imino]-5-bromacenaphthene (Dpp-Br-Bian) (L<sup>1</sup>) and 1,2-bis[(4-bromo-2,6-diisopropylphenyl)imino]-5-bromacenaphthene (*p*-Br-Dpp-Br-Bian) (L<sup>2</sup>), respectively. Compounds L<sup>1</sup> and L<sup>2</sup> act as neutral ligands in the [(Dpp-Br-Bian)ZnCl<sub>2</sub>] (I), [(*p*-Br-Dpp-Br-Bian)AlCl<sub>3</sub>] (III), and [(*p*-Br-Dpp-Br-Bian)GaCl<sub>3</sub>] (IV) complexes synthesized by the reactions of free diimines with the corresponding metal chlorides. The reaction of the known dibromosubstituted derivative 1,2-bis[(4-bromo-2,6-di-*iso*-propylphenyl)iminoacenaphthene (*p*-Br-Dpp-Bian) (L<sup>3</sup>) with copper(I) chloride also affords complex [(*p*-Br-Dpp-Bian)CuCl] (II) with the neutral diimine ligand. New compounds L<sup>1</sup>, L<sup>2</sup>, and I–IV are characterized by NMR, IR spectroscopy, and elemental analysis. The molecular structure of complex I is determined by X-ray structure analysis.

*Keywords:* bromine, redox-active ligands, bis(arylimino)acenaphthenes, molecular structure, zinc, copper, aluminum, gallium, complexes

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## **INTRODUCTION**

Diimines, including conformationally rigid bis(arylimino)acenaphthenes (Ar-bian), are widely used as chelating ligands during the last decades in the chemistry of transition and nontransition metals. Although the first reports on them appeared in the 1990s [1-4], the study of these ligands is presently one of the priority trends in the chemistry of coordination compounds, since the Lewis acidity of the related metal complexes and, correspondingly, their reactivity can be purposefully controlled due to the possibility of varying the organic substituent at the nitrogen atom. Numerous complexes of transition and nontransition complexes based on Ar-bian [5] in which the ligand can be in the neutral, mono-, di-, tri-, and tetraanionic [6] states have been reported to the present time. Many of these compounds were used as efficient catalysts in the organic synthesis reactions [7-22] and in the polymerization of olefins [23-33] and cyclic esters [34 - 38].

In spite of great interest in using Ar-bian ligands in coordination chemistry, only several representatives of the bromosubstituted derivatives of this series are met in the literature. In all cases, the bromine atoms are located in the *para* positions of the aryl substituent at the nitrogen atom [24, 39, 40]. The nickel derivatives based on p-Br-Dpp-bian are efficient catalysts for alkene polymerization [27, 28]. Taking into account this fact together with the data on the unique properties of the nontransition metal complexes with bis(arylimino)acenaphthenes, such as the reversible cycloaddition of alkynes [16, 41], isothiocyanates [42], and isocyanates [43] to the binuclear derivatives [(Dpp-bian)M-M(Dpp-bian)] (M = Ga, Al), the capability of the gallium complex of undergoing the two-electron oxidative addition of the substrate similarly to the transition metals [44] and the capability of the magnesium complex of one-electron reducing organic halides and aromatic ketones [45, 46], we believe that the synthesis of new bromosubstituted ligands of the Ar-bian series is promising. These ligands are interesting from the point of view of metallocomplex catalysis and also as precursors for the synthesis of new acenaphthene-1,2-diimine derivatives. The further functionalization of Ar-bian would provide their capability of forming 2D, 3D, and polymer frameworks as a result of binding the functional groups with the metal atoms due to both the redoxactive diimine fragment and redox-inactive functional groups. This seems perspective for the construction of metal-organic frameworks (MOFs) based on redoxactive organic ligands, examples of which are fairly rare [47-49].

In this work, we report the synthesis of mono-, di-, and tribromosubstituted bis(arylimino)acenaphthenes and the related zinc, copper(I), aluminum, and gallium complexes. Acenaphthene-1,2-diimines containing bromine atoms in the naphthalene moiety were synthesized for the first time.

### **EXPERIMENTAL**

Compounds **I–IV** are sensitive of oxygen and moisture and, hence, all manipulations on their synthesis and identification were conducted in vacuo using the Schlenk technique or in a nitrogen atmosphere (Glovebox M. Braun). Toluene (Aldrich) was dried and stored over sodium benzophenone. Pentane (Aldrich) was dried over a sodium mirror and sampled by condensation in vacuo prior to use. Other solvents and reagents used for the synthesis of the organic compounds were purified using commonly accepted procedures. Deuterobenzene (Aldrich) was dried over sodium benzophenone and sampled by condensation in vacuo into NMR tubes containing samples of the studied compounds. 5-Bromacenaphthene was synthesized using the published procedure [50].

IR spectra were recorded on an FSM-1201 spectrometer in a range of 4000–450 cm<sup>-1</sup> (samples in Nujol). <sup>1</sup>H NMR spectra were detected on Bruker DPX-200 (200 MHz) and Bruker Avance III (400 MHz) spectrometers. Melting points were determined in sealed evacuated capillaries. Elemental analyses were carried out by the combustion of samples in oxygen using the Pregel method.

**Synthesis of 4-bromo-2,6-di-***iso***-propylaniline.** Bromine (12.1 g, 75.6 mmol) was added within 10 min to a solution of 2,6-di-*iso*-propylaniline (13.4 g, 75.7 mmol) in an ethanol—acetic acid (2 : 1) mixture (60 mL). The reaction mixture was stirred at room temperature for 2 h. After the end of the reaction, a 20% aqueous solution of NaOH was added to the mixture until a weakly alkaline pH was achieved. The organic layer was extracted with diethyl ether (25 mL), washed with water two times, and kept over magnesium sulfate for 15 h. After the ether was removed, a red-violet oily liquid of 4-bromo-2,6-di-*iso*-propylaniline was formed. The yield was 18.9 g (97%).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 300 K; *J*, Hz),  $\delta$ , ppm: 7.17 (s, 2H), 3.87 (s, 2H), 2.92 (sept, 4H, *J* = 6.8), 1.29 (d, 12H, *J* = 6.8).

IR (v, cm<sup>-1</sup>): 3492 w, 3405 w, 2360 w, 2337 w, 1620 m, 1575 w, 1243 w, 1209 w, 866 m, 838 w, 670 w. The spectra correspond to the published data [51].

Synthesis of 5-bromacenaphthenequinone. Sodium bichromate dihydrate (23.9 g, 80.2 mmol) was added by small portions with continuous stirring to a solution of 5-bromacenaphthene (11.0 g, 47.2 mmol) and cesium chloride heptahydrate (0.5 g, 1.3 mmol) in acetic acid (50 mL) at 40°C for 1 h. The reaction mixture was stirred at 40°C for 8 h, and cold water (1 L)

was added. The precipitate formed was filtered off on the Büchner funnel and washed with water. The formed solid substance with a 10% solution of soda (200 mL) was stirred at 80°C for 30 min, separated by filtration on the Büchner funnel, and washed with water. The precipitate was extracted with a 4% aqueous solution of sodium bisulfate (500 mL) at 80°C for 30 min. The obtained filtrate was acidified with concentrated sulfuric acid with permanent stirring to reach a weakly acidic pH of the solution. The precipitated yellow substance was filtered off, consecutively washed with water and ethanol, and dried in vacuo. The yield was 9.4 g (76%), mp > 238 (decomp.).

<sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>, 300 K; *J*, Hz),  $\delta$ , ppm: 8.37 (d, 1H, *J* = 8.2), 8.24–8.09 (m, 2H), 8.04 (d, 1H, *J* = 7.6), 7.93 (d, 1H, *J* = 7.2).

IR (v, cm<sup>-1</sup>): 2362 w, 1730 s, 1684 w, 1604 w, 1576 w, 1507 w, 1304 w, 1268 w, 1209 w, 1117 w, 1083 w, 1020 m, 943 w, 897 w, 847 w, 818 w, 794 w, 768 m, 724 w.

Synthesis of Dpp-Br-bian (L<sup>1</sup>). 5-Bromoacenaphthenequinone (3.0 g, 11.5 mmol) in acetic acid (50 mL) was heated to 118°C. A solution of 2,6-di-*iso*propylaniline (4.1 g, 23.1 mmol) in acetic acid (5 mL) was added dropwise with permanent stirring to the obtained hot solution for 1 h. As aniline was added, the precipitate of 5-bromacenaphthenequinone was dissolved and the solution turned dark red. The reaction mixture was refluxed for 4 h and then kept at 5°C for 24 h. The red precipitate formed was filtered off from the solution, consecutively washed with water, ethanol, hexane, and diethyl ether, and dried in vacuo. The yield was 5.6 g (84%), mp > 265 (decomp.).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K; *J*, Hz),  $\delta$ , ppm: 8.10 (d, 1H, *J* = 8.3), 7.62 (d, 1H, *J* = 7.3), 7.48 (pt, 1H), 7.31–7.27 (m, 5H), 6.68 (d, 1H, *J* = 7.3), 6.45 (d, 1H, *J* = 7.8), 3.00 (sept, 4H, *J* = 6.8), 1.24 (d, 12H, *J* = 6.8), 0.98 (d, 6H, *J* = 4.3), 0.97 (d, 6H, *J* = 4.3).

IR (v, cm<sup>-1</sup>): 1743 w, 1673 w, 1654 m, 1631 s, 1579 m, 1523 m, 1425 m, 1361 w, 1348 w, 1324 m, 1270 w, 1237 w, 1223 w, 1188 m, 1167 w, 1108 w, 1091 m, 1043 m, 1022 m, 975 w, 960 w, 938 w, 890 w, 875 w, 862 s, 836 m, 816 w, 803 w, 781 s, 746 m, 726 w.

For C <sub>42</sub> H <sub>45</sub> N <sub>2</sub> Br	For	C	-H₄	5N/	Br
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Anal. calcd., %	C, 76.70	H, 6.90
Found, %	C, 76.67	H, 6.88

Synthesis of *p*-Br-Dpp-Br-bian (L<sup>2</sup>). A solution of 5-bromacenaphthenequinone (3.0 g, 11.5 mmol) in acetic acid (50 mL) was heated to  $118^{\circ}$ C. A solution of 4-bromo-2,6-di-*iso*-propylaniline (6.0 g, 23.4 mmol) in acetic acid (5 mL) was added dropwise for 1 h with permanent stirring to the obtained hot solution. As aniline was added, the precipitate of 5-bromacenaph-thenequinone was dissolved and the solution turned

dark red. The reaction mixture was refluxed for 4 h and then kept at  $+5^{\circ}$ C for 24 h. The red precipitate formed was separated from the solution by filtration, consecutively washed with water, ethanol, hexane, and diethyl ether, and dried in vacuo. The yield was 5.7 g (67%), mp > 215 (decomp.).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K; *J*, Hz),  $\delta$ , ppm: 8.16 (d, 1H, *J* = 8.5), 7.69 (d, 1H, *J* = 7.8), 7.55 (pt, 1H, *J* = 7.6) 7.39 (s, 2H), 7.38 (s, 2H), 6.83 (d, 1H, *J* = 7.0), 6.61 (d, 1H, *J* = 7.8), 2.93 (sept, 4H, *J* = 6.8), 1.21 (d, 12H, *J* = 7.0), 0.97 (d, 6H, J = 4.7), 0.95 (d, 6H, *J* = 4.7).

IR (v, cm<sup>-1</sup>): 1711 s, 1676 m, 1633 m, 595 w, 1582 w, 1571 w, 1327 m, 1291 m, 1271 w, 1236 w, 1209 w, 1187 m, 1171 w, 1148 w, 1093 w, 1047 w, 1029 w, 970 w, 942 w, 924 w, 865 m, 846 w, 824 w, 781 m, 750 w, 728 m, 627 w, 478 w.

For C<sub>42</sub>H<sub>43</sub>N<sub>2</sub>Br<sub>3</sub>

Anal. calcd., %	C, 61.86	H, 5.31
Found, %	C, 61.85	H, 5.28

Synthesis of *p*-Br-Dpp-bian (L<sup>3</sup>). A solution of acenaphthenequinone (5.0 g, 27.5 mmol) in acetic acid (50 mL) was heated to 118°C. A solution of 4-bromo-2,6-di-*iso*-propylaniline (14.5 g, 56.6 mmol) in acetic acid (5 mL) was added dropwise for 1 h with permanent stirring to the obtained hot solution. As aniline was added, the precipitate of acenaphthenequinone was dissolved and the solution turned dark red. The reaction mixture was refluxed for 4 h and then kept at +5°C for 24 h. The orange precipitate formed was separated from the solution by filtration, consecutively washed with water, ethanol, hexane, and diethyl ether, and dried in vacuo. The yield was 14.3 g (79%).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 300 K; *J*, Hz),  $\delta$ , ppm: 7.93 (d, 2H, *J* = 8.3), 7.50–7.33 (m, 6H), 6.78 (d, 2H, *J* = 7.1), 2.96 (sept, 4H, *J* = 6.8), 1.21 (d, 12H, *J* = 6.8), 0.96 (d, 12H, *J* = 6.8).

IR (v, cm<sup>-1</sup>): 1722 m, 1678 w, 1649 m, 1597 w, 1324 w, 1277 m, 1235 w, 1189 w, 1039 w, 1015 w, 944 w, 924 w, 862 m, 835 m, 822 w, 785 m, 722 w.

Synthesis of [(Dpp-Br-bian)ZnCl<sub>2</sub>] (I). Zinc chloride (0.06 g, 0.5 mmol) was added to a solution of compound L<sup>1</sup> (0.29 g, 0.5 mmol) in toluene (20 mL). The mixture was stirred at 60°C for 2 h. The obtained orange solution was kept at 10°C for 24 h. The precipitated orange crystals were decanted from the solution, washed with cold toluene, and dried in vacuo. The yield of compound I was 0.33 g (86%).

<sup>1</sup>H NMR (200 MHz,  $C_6D_6$ , 298 K; *J*, Hz),  $\delta$ , ppm: 7.62–7.50 (m, 1H), 7.30–7.17 (m, 6H), 7.15–6.97 (m, 5H), 6.70 (d, 1H, *J* = 7.8), 6.62–6.55 (m, 2H), 6.28 (d, 1H, *J* = 7.8), 3.77–3.55 (m, 4H), 2.11 (s, 3H), 1.47 (d, 12H, *J* = 6.4), 0.82 (d, 6H, *J* = 2.8), 0.79 (d, 6H, *J* = 2.8). IR (v, cm<sup>-1</sup>): 1661 s, 1625 s, 1593 m, 1572 s, 1495 m, 1417 m, 1397 w, 1365 w, 1347 m, 1326 m, 1277 m, 1253 m, 1220 m, 1208 m, 1185 m, 1170 w, 1130 m, 1118 m, 1106 w, 1096 w, 1074 w, 1043 w, 1032 s, 974 s, 954 m, 937 m, 854 s, 823 m, 800 s, 785 s, 759 s, 729 s, 695 s, 661 m, 622 m, 594 w, 577 w, 564 w, 527 m, 486 m, 466 m.

For C <sub>41.50</sub> H <sub>45</sub> N <sub>2</sub> Cl <sub>2</sub>	BrZn	
Anal. calcd., %	C, 63.53	H, 5.71
Found, %	C, 63.48	H, 5.68

Synthesis of [(p-Br-Dpp-bian)CuCl] (II). Copper(I) chloride (0.05 g, 0.5 mmol) was added to a solution of compound L<sup>3</sup> (0.32 g, 0.5 mmol) in toluene (20 mL). The mixture was stirred at 60°C for 3 h. The resulting blue solution was kept at 10°C for 24 h. The precipitated blue crystals were decanted from the solution, washed with cold toluene, and dried in vacuo. The yield of compound II was 0.30 g (81%).

<sup>1</sup>H NMR (200 MHz,  $C_6D_6$ , 298 K; *J*, Hz),  $\delta$ , ppm: 7.58 (s, 4H), 7.20–7.11 (m, 2H), 6.83 (d, 2H, *J* = 6.4), 6.64 (pt, 2H), 3.42 (sept, 4H, *J* = 6.4), 1.28 (d, 12H, *J* = 6.4), 0.76 (d, 12H, *J* = 6.4).

IR (v, cm<sup>-1</sup>): 1645 s, 1603 w, 1573 m, 1494 w, 1365 w, 1327 s, 1281 m, 1232 w, 1223 m, 1187 s, 1149 w, 1118 m, 1086 w, 1072 w, 1043 m, 1030 w, 943 m, 923 w, 888 w, 865 s, 845 w, 829 m, 819 s, 797 w, 776 s, 729 s, 694 s, 617 m, 533 m, 499 w, 465 s.

For C42H44N2ClBr2Cu

Anal. calcd., %	C, 60.37	H, 5.31
Found, %	C, 60.34	H, 5.29

Synthesis of  $[(p-Br-Dpp-Br-bian)AlCl_3]$  (III). A mixture of diimine L<sup>2</sup> (0.25 g, 0.34 mmol) and AlCl<sub>3</sub> (0.045 g, 0.34 mmol) in toluene (5 mL) was stirred at 60°C overnight. Pentane (20 mL) was added to the obtained dark orange solution. Orange crystals precipitated from a toluene–pentane (9 : 1) mixture. The yield of compound III was 0.21 g (62%).

<sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 298 K; *J*, Hz),  $\delta$ : 7.61 (d, 1H, *J* = 8.3), 7.52 (d, 4H, *J* = 8.5), 6.82 (d, 1H, *J* = 7.5), 6.77 (d, 1H), 6.65 (pt, 1H, *J* = 7.8), 6.46 (d, 1H, *J* = 7.8), 2.94 (br.s, 4H), 1.15 (d, 6H, *J* = 6.3), 1.14 (d, 6H, *J* = 6.3), 0.8 (d, 6H, *J* = 6.8), 0.77 (d, 6H, *J* = 6.8).

IR (v, cm<sup>-1</sup>): 1674 m, 1661 m, 1634 m, 1595 m, 1574 s, 1423 m, 1418 m, 1366 m, 1348 w, 1319 s, 1265 m, 1221 m, 1207 w, 1186 m, 1152 m, 1071 m, 1030 m, 972 s, 943 m, 889 w, 876 m, 864 m, 845 w,

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Parameter	Value
Empirical formula	$C_{41,50}H_{45}BrCl_2N_2Zn$
FW	787.97
Crystal system	Trigonal
Space group	$R\overline{3}$
Temperature, K	298(2)
Radiation wavelength, Å	0.71073
<i>a</i> , Å	23.0682(4)
<i>b</i> , Å	23.0682(4)
c, Å	39.1825(8)
α, deg	90
β, deg	90
γ, deg	120
$V, Å^3$	18057.2(7)
Ζ	18
$\rho_{calc}, g/cm^3$	1.304
$\mu$ , mm <sup>-1</sup>	1.770
<i>F</i> (000)	7326
Crystal size, mm	$0.28 \times 0.22 \times 0.18$
Measurement range over $\theta$ , deg	2.89-26.37
Indices of ranges	$-28 \le h \le 28,$
	$-28 \le k \le 28,$
	$-48 \le l \le 48$
Number of measured reflections	85468
Number of independent reflections $(R_{int})$	8148 (0.0483)
Number of reflections with $I > 2\sigma(I)$	5551
Absorption correction (max/min)	0.779/0.696
Data/restraints/parameters	8148/92/490
GOOF	1.064
$R_1, wR_2 (I \ge 2\sigma(I))$	0.0579, 0.1535
$R_1$ , $wR_2$ (for all reflections)	0.0905, 0.1724
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}, e {\rm \AA}^{-3}$	0.920/-0.861

**Table 1.** Crystallographic data and experimental and structure refinement parameters for compound I

822 s, 806 w, 789 m, 72	'9 s, 741 m	1, 638 w, 61	l w, 604 w,
529 w, 496 vs, 484 vs.			

C, 56.92	H, 5.06
C, 56.93	H, 4.98
	C, 56.92 C, 56.93

Synthesis of  $[(p-Br-Dpp-Br-bian)GaCl_3]$  (IV). A mixture of diimine L<sup>2</sup> (0.25 g, 0.34 mmol) and GaCl<sub>3</sub> (0.060 g, 0.34 mmol) in toluene (5 mL) was stirred at

Table 2. Selected bond lengths (Å) and bond angles (deg) in compound I

Bond	d, Å
Zn(1)–N(1)	2.123(3)
Zn(1) - N(2)	2.135(3)
Zn(1)-Cl(1)	2.1905(14)
Zn(1)-Cl(2)	2.1861(13)
N(1)-C(1)	1.273(5)
N(2)–C(2)	1.269(5)
C(1)–C(2)	1.522(5)
Br(1) - C(8)	1.917(4)
Angle	ω, deg
N(1)ZnN(2)	79.86(11)
Cl(2)Zn(1)Cl(1)	122.39(6)

 $60^{\circ}$ C overnight. All volatiles were removed in vacuo, and diethyl ether (5 mL) was added. Orange crystals precipitated from the ether solution. The yield of compound **IV** was 0.24 g (65%).

<sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 298 K; *J*, Hz),  $\delta$ , ppm: 7.69 (br.s, 1H), 7.64 (d, 4H, *J* = 5.3), 6.86 (br.s, 1H), 6.77 (br.s, 1H), 6.52 (br.s, 1H), 6.15 (br.s, 1H), 3.27 (br.s, 2H), 2.94 (br.s, 2H), 1.20 (br.s, 12H), 0.81 (br.s, 6H), 0.61 (br.s, 6H).

IR (v, cm<sup>-1</sup>): 1661 m, 1613 m, 1587 w, 1570 m, 1418 m, 1366 s, 1350 m, 1321 m, 1304 w, 1277 w, 1234 w, 1221 w, 1207 w, 1182 m, 1171 w, 1152 w, 1125 w, 1092 w, 1071 w, 1061 w, 1036 w, 976 m, 943 w, 889 w, 864 m, 847 m, 822 m, 797 w, 785 m, 775 m, 750 m, 739 m, 698 w, 667 w, 631 w, 556 w, 532 w, 453 w, 403 w.

For C<sub>43</sub>H<sub>45</sub>N<sub>2</sub>Cl<sub>3</sub>Br<sub>3</sub>Ga

Anal. calcd., %	C, 56.92	H, 5.06
Found, %	C, 56.64	H, 5.05

**X-ray structure analysis of compound I.** The crystals of compound I suitable for X-ray diffraction analysis were obtained by crystallization from toluene. The crystal chosen for analysis was covered with a mineral oil (Aldrich), fixed on a glass capillary, and then placed in a cold nitrogen flow of an Agilent Xcalibur E diffractometer ( $\omega$  scan mode, Mo $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å). Experimental sets of intensities were integrated using the CrysAlisPro program [52]. The structure was solved by a direct method and refined by full-

matrix least squares for  $F_{hkl}^2$  using the SHELXTL program package [53] in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined isotropically. An absorption correction was applied using the SCALE3 ABSPACK program [54]. The bromine and hydrogen atoms were disordered over positions 5



Fig. 1. <sup>1</sup>H NMR spectrum of compound  $L^1$  (400 MHz, CDCl<sub>3</sub>, 298 K).

and 6 of the acenaphthene fragment. The solvate molecules of toluene and benzene in the partial positions (on the inversion center and on the rotation axis  $C_3$ , respectively) were found in the crystal of compound **I**. The main crystallographic characteristics and the experimental parameters of X-ray structure analysis for compound **I** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The structure of compound I was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1957209; ccdc.cam.ac.uk/getstructures).

#### **RESULTS AND DISCUSSION**

5-Bromoacenaphthenequinone (76%) was synthesized by the oxidation of 5-bromoacenaphthene with sodium bichromate in acetic acid in the presence of cerium chloride (40°C, 9 h). The compound was characterized by NMR and IR spectroscopy. The subsequent condensation of 5-bromoacenaphthenequinone with 2,6-di-*iso*-propylaniline in a ratio of 1 : 2 in acetic acid (118°C, 4 h) (Scheme 1) gave 1,2-bis[(2,6-di-isopropylphenyl)imino]-5-bromoacenaphthene monobromosubstituted at the naphthalene moiety (Dpp-Br-bian) ( $L^1$ ). The reaction product was isolated as a finely crystalline red powder in a yield of 84%. A similar reaction of 5-bromoacenaphthenequinone with 4-bromo-2,6-di-iso-propylaniline afforded the tribromosubstituted derivative 1,2-bis[(4-bromo-2,6-diisopropylphenyl)imino]-5-bromoacenaphthene ( $L^2$ ) as a finely crystalline red substance in a yield of 67%



Fig. 2. <sup>1</sup>H NMR spectra of compounds (a) I, (b) II, and (c) III ((a, b) 200 and (c) 400 MHz,  $C_6D_6$ , 298 K).

(Scheme 1). Note that bis(arylimino)acenaphthenes bromosubstituted at the naphthalene moiety were synthesized for the first time. The condensation

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of 4-bromo-2,6-di-*iso*-propylaniline with unsubstituted acenaphthenequinone gave the known compound 1,2-bis[(4-bromo-2,6-di-*iso*-propylphenyl)imino]acenaphthene (L<sup>3</sup>) [28]. However, acetic acid was used as a solvent instead of toluene, which shortened the reaction time from 3 days to 4 h. The synthesis of compounds  $L^1-L^3$  is presented in Scheme 1.





The IR spectra of new compounds  $L^1$  and  $L^2$  exhibit absorption bands at 1654, 1632 cm<sup>-1</sup> ( $L^1$ ) and 1711, 1676 cm<sup>-1</sup> ( $L^2$ ) corresponding to stretching vibrations of the C=N double bonds.

The <sup>1</sup>H NMR spectrum of compound L<sup>1</sup> (Fig. 1) contains signals of the *iso*-propyl groups of the 2,6*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituents: the doublet of the doubled intensity ( $\delta$  1.24 (12H) ppm) and two overlapped doublets ( $\delta$  0.98 (6H) and 0.97 (6H) ppm) of the protons of eight methyl groups and the septet of the doubled intensity ( $\delta$  3.00 (4H) ppm) of four methine protons. The signals of five protons of the naphthalene moiety diverge and appear as four doublets ( $\delta$  8.10 (1H), 7.62 (1H), 6.68 (1H), and 6.45 (1H) ppm) and the pseudo-triplet at  $\delta$  7.48 (1H) ppm. The aromatic protons of the 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituents are presented by the multiplet in a range of 7.31–7.27 (5H) ppm. The <sup>1</sup>H NMR spectrum of compound L<sup>2</sup> exhibits the same set of signals as that for compound L<sup>1</sup>: the methine protons of the *iso*-propyl substituents appear as the septet at  $\delta$  2.93 (4H) ppm, and the protons of the methyl groups of the *iso*-propyl substituents are observed as two overlapped doublets ( $\delta$  0.97 (6H), 0.95 (6H) ppm) and the doublet of the doubled intensity at  $\delta$  1.21 ppm (12H). Unlike compound L<sup>1</sup>, the aromatic protons of the 4-Br-2,6-*i*Pr<sub>2</sub>-C<sub>6</sub>H<sub>2</sub> substituents in complex L<sup>2</sup> are presented by two singlets at  $\delta$ 7.39 (2H) and 7.38 (2H) ppm. The signals of the protons of the naphthalene moiety are observed as four doublets at  $\delta$  8.16 (1H), 7.69 (1H), 6.83 (1H), and 6.61 (1H) ppm and the pseudotriplet at  $\delta$  7.55 (1H) ppm.

The reaction of compound  $L^1$  with zinc chloride (Scheme 2) occurs in toluene at 60°C for 2 h. Orange crystals of compound [(Dpp-Br-bian)ZnCl<sub>2</sub>] (I) were obtained by keeping the reaction mixture at 10°C for 24 h (86% yield).



The <sup>1</sup>H NMR spectrum of compound **I** in deuterobenzene (Fig. 2a) contains the same set of signals as free bis(imino)acenaphthene L<sup>1</sup>. The signals of the protons of the methyl groups of the  $2,6-iPr_2C_6H_3$  substituents of complex I: two overlapped doublets at  $\delta 0.82$  (6H) and 0.79 (6H) ppm, the doublet at  $\delta 1.47$  (12H) ppm, and the multiplet of overlapped signals of the methine protons ( $\delta 3.77-3.55$  (4H) ppm). The doublets at  $\delta 6.28$  (1H)

and 6.70 (1H) ppm and the signals in ranges of  $\delta$  6.55– 6.62 (2H), 7.17–7.30 (6H), and 7.50–7.62 (1H) ppm are assigned to the aromatic protons of the naphthalene fragment and phenyl substituents at the nitrogen atoms. The crystalline cell of compound **I** contains the toluene molecule, whose signals are presented by the multiplet at  $\delta$  7.15–6.97 (5H) and the singlet at  $\delta$  2.11 (3H) ppm.

The reaction of compound  $L^3$  with copper(I) chloride (Scheme 3) occurs in toluene at 60°C for 3 h. The blue crystals of complex [(p-Br-Dpp-bian)CuCl] (II) were obtained by keeping the reaction mixture at 10°C for 24 h (81% yield).

In the IR spectra of complexes I and II, the intense absorption bands characteristic of the C=N bond vibrations are observed at 1661 and 1625 cm<sup>-1</sup> and at 1645 cm<sup>-1</sup>, respectively, indicating the neutral form of the diimino ligand in these compounds.



Since the molecule of compound II is symmetric, the <sup>1</sup>H NMR spectrum of the complex (Fig. 2b) is simpler than the spectrum of complex I with the nonsymmetric ligand. The <sup>1</sup>H NMR spectrum of compound II exhibits the signals of the 4-Br-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>2</sub> substituents: two doublets ( $\delta$  0.76 (12H) and 1.28 (12H) ppm), the septet at  $\delta$  3.42 (4H) ppm of the *iso*propyl group, and the singlet at  $\delta$  7.58 (4H) ppm of the aromatic protons. The multiplet at  $\delta$  7.20–7.11 (2H), doublet at  $\delta$  6.83 (2H), and pseudotriplet at  $\delta$  6.64 (2H) ppm are assigned to the protons of the naphthalene moiety.

The reactions of aluminum and gallium chlorides with diimine  $L^2$  (Scheme 4) in toluene afford compounds [(*p*-Br-Dpp-Br-bian)AlCl<sub>3</sub>] (III) and [(*p*-Br-Dpp-Br-bian)GaCl<sub>3</sub>] (IV) obtained as orange crystals from pentane in 62 and 65% yields, respectively.



The <sup>1</sup>H NMR spectra of compounds III and IV are fairly complicated because of the nonsymmetric structures of these compounds. For example, the <sup>1</sup>H NMR spectrum of complex IV (Fig. 2c) contains five signals of five nonequivalent protons of the naphthalene moiety of the ligand: the doublets at  $\delta$  7.61, 6.82, 6.77, and 6.46 and the pseudotriplet at 6.65 ppm. The doublet at  $\delta$  7.52 ppm (4H) is assigned to the protons of the phenyl substituents at the nitrogen atoms, the broadened singlet at 2.94 ppm (4H) is ascribed to the methine protons of the isopropyl groups, and four doublets at 1.15, 1.14, 0.8, and 0.77 ppm (6H each) are attributed to the protons to the CH<sub>3</sub> groups of the *iso*propyl substituents. The NMR spectrum of compound IV contains a similar set of signals. The IR spectra of complexes III and IV are characteristic of the neutral form of the Ar-bian ligand: the absorption bands at 1674, 1661 cm<sup>-1</sup> (III) and 1661 cm<sup>-1</sup> (IV), respectively, correspond to stretching vibrations of the C=N double bonds.

According to the X-ray structure analysis data of complex I (Fig. 3), the coordination environment of the zinc atom is a distorted tetrahedron. The bond lengths in the diimine fragment (N(1)–C(1) 1.273(5), N(2)–C(2) 1.269(5), and C(1)–C(2) 1.522(5) Å) confirm the neutral state of the Dpp-Br-bian ligand. For comparison, the N(1)–C(1), N(2)–C(2), and C(1)–C(2) distances in the [(Cybu-bian)ZnCl<sub>2</sub>] derivative (Cybu is cyclobutyl) with neutral diimine are 1.282(3), 1.278(3), and 1.526(3) Å, respectively [55]. At the

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No. 4



**Fig. 3.** Molecular structure of compound **I**. Thermal ellipsoids of 30% probability. Hydrogen atoms are omitted.

same time, these distances are 1.377(3), 1.380(3), 1.362(3) and 1.3244(17), 1.3357(15), 1.4414(18) Å [57] compounds [{(Dpp-bian)Zn-Ga(Dppin bian) $\{K(Thf)_{5}\}$  [56] and [(Dpp-bian)Zn-Zn(Dppbian)] with the dianionic and radical-anionic ligands, respectively. The Zn-N(1) and Zn-N(2) bonds in complex I (2.123(3) and 2.135(3) Å) are appreciably longer than the Zn–N distances in similar neutral zinc bis(alkylimino)acenaphthene complexes [(Cybubian)ZnCl<sub>2</sub>] (2.081(2) and 2.085(2) Å) and [(Norbbian)ZnCl<sub>2</sub>] (Norb is norbornyl) (2.093(5) and 2.096(5) Å) [55] but are well consistent with those in compound [(Dpp-bian)ZnCl<sub>2</sub>] (2.111(2))and 2.110(2) Å) [58]. These differences can be explained by a steric hindrance caused by the  $2,6-iPr_2C_6H_3$  substituents at the nitrogen atoms.

Thus, we synthesized for the first time bis(arylimino)acenaphthenes bromosubstituted in the naphthalene ring and some related metal complexes. These acenaphthene-1,2-diimines are convenient precursors for the further preparation of functionalized compounds, for example, carboxyl-substituted Ar-bian. The introduction of functional groups can provide the formation of polymer frameworks due to binding adjacent molecules through metal atoms. This feature makes them to be convenient reagents for the preparation of metal-organic frameworks (MOFs) containing redox-active organic diimine fragments. These compounds would possibly manifest the properties that are presently unknown for MOFs, for example, the capability of reversible switching spectral and magnetic characteristics and of controlled regulating the reactivity due to a tuned change in the charge distribution between the metal and redox-active organic ligand.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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