# Synthesis and Electrochemical Properties of 2,5-Disubstituted Derivatives of 1,4-Bis(4,5-diphenylidimidazol-2-yl)benzene

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**Abstract**—The data on the synthesis and electrochemical properties of 2,5-disubstituted derivatives of 1,4-bis(4,5-diphenyldimidazol-2-yl)benzene are reported. The effect of substituents on redox properties has been comprehensively investigated. The electrochemical reduction of quinones into the biradical occurs at positive potentials and is a result of two stages of single-electron transfer, through the stage of the monoradical formation. The correlation between the reduction potentials and the salts structure has been found.

Keywords: biradicals, monoradicals, cyclic voltammetry, 1,4-bis(4,5-diphenyldimidazol-2-yl)benzene

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Monoradicals of the triarylimidazoles series are convenient and widely used objects for the investigation of correlation between structure and reactivity of stable radicals, due to their high stability against atmospheric oxygen [1–3]. However, biradicals of this series have been scarcely studied so far.

We have earlier synthesized bisimidazole systems with imidazole fragments at 1,4- positions of benzene ring, oxidation of which have yielded quinones exhibiting paramagnetic susceptibility at heating, due to the rupture of quinoid bonds. It has been suggested that substitution of the benzene ring at the o-position with respect to imidazole moiety should prevent the formation of quinoid systems, and the so obtained biradical products should possess unusual redox properties. Herein we present the approaches to the synthesis of 2-bromo and 2,5-dibromo derivatives of 1,4-bis(4,5-diphenylimidazol-2-yl)benzene, the simplest diimidazoles. Electrochemical properties of the obtained compounds were studied by means of cyclic voltammetry. It was shown that steric tension caused by two bromine atoms at the central ring was responsible for the unusual redox properties, in particular, the shift of the potential of the reduction process to more positive potentials. The obtained values of the reduction potentials for 2,5-disubstituted derivatives of 1,4-bis(4,5-diphenylimidazol-2-yl)benzene were extreme for 1,4-subtituted cyclohexadienes.

2,5-Disubstituted-1,4-bis(4,5-diphenylimidazol-2-yl)benzenes were synthesized as shown in Scheme 1.

Starting mono- and dibromo-substituted *para*-xylenes required for the synthesis of dialdehydes **1b** and **1c** were synthesized as described elsewhere [4, 5]. The obtained dialdehydes **1a–1c** were used for the synthesis of diimidazoles **2a–2c** which were oxidized into quinones **3a–3c**.

Oxidation of imidazoles was performed using potassium hexacyanoferrate(III) in a biphasic benzene– water system in the presence of potassium hydroxide (Scheme 2). Quinones were separated as precipitates partially soluble in benzene. According to the results of TLC (Silufol, benzene as eluent), imidazoles were not completely oxidized under the process conditions, since the oxidation products contained the starting imidazole along with unidentified products.

To elucidate the influence of the substitution of the central ring on the properties of quinones 3a-3c, we studied their electrochemical behavior by means of cyclic voltammetry. The measurements were conducted using Pt electrode in CH<sub>3</sub>CN. Cyclic voltammogram (CV) of compound 3a is shown in Fig. 1. A single two-electron

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2a-2c

$$R^{1} = R^{2} = H(a); R^{1} = H, R^{2} = Br(b); R^{1} = R^{2} = Br(c).$$

Scheme 2.



 $R^{1} = R^{2} = H(a); R^{1} = H, R^{2} = Br(b); R^{1} = R^{2} = Br(c).$ 

wave was observed over the range of potentials between 1 and -1 V (at E = 0.17 V vs. Ag/AgCl/KCl) with diffusion current limitation. An oxidation peak present at the reverse semi-cycle indicated the reversibility of the reduction process. The said peak was present even at low scan rates, reflecting high stability of the formed specie. Hence, the species particles formed upon electrochemical



Fig. 1. Cyclic voltammogram of compound 3a (1 mM, Pt, CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, 100 mV/s).

reduction were stable over time and did not undergo any chemical transformations.

It should be noted that the processes of electrochemical reduction accompanied by the transfer of two electrons at the same potential are rare, being possible in certain cases only. For example, if the second electron is transferred at more positive potential than the first one, it could look like a two-electron process. Another option is the transfer of the first electron directly followed by very fast chemical reaction (in the case of quinone this is possible at certain pH values of pH) [6]. In this case, the voltamperogram shape is changed: the peak becomes narrower, the peak potential difference of direct and reverse processes is up to 28 mV, and the peak current is increased [6]. When two identical redox centers are separated by a spacer, mere addition of currents can be observed, and the curve shape remains almost unchanged. The latter case was observed for the CV shown in Fig. 1. Therefore, the two-electron behavior of the reduction wave could be explained as follows: the anion-radical formed at the first stage quickly detached a proton from the solvent



Fig. 2. Cyclic voltammogram of compound 3b (1 mM, Pt,  $CH_2Cl_2$ , 0.1 M  $Bu_4NPF_6$ ).

(in other words, got protonated) and was immediately reduced into the anion-radical at the same potential, the latter undergoing various chemical transformation, for example, protonation (Scheme 3).

That series of sequential electrochemical and chemical processes could be described as the ECEC mechanism (electrochemical, chemical, electrochemical, and chemical stages). However, such mechanism should lead to irreversible reduction waves, since the electrochemical stage is followed by the chemical one, whereas reversible wave was observed during the CV scan in our study (Fig. 1). Hence, the said scheme of electrochemical process was not consistent with the obtained experimental



Fig. 3. Cyclic voltammogram of compound 3c (1 mM, Pt,  $CH_2Cl_2$ , 0.1 M  $Bu_4NPF_6$ ).

data. Apparently, dianion of 3a compound which was oxidized during the reverse CV scan should be formed via a different mechanism. It could be suggested that the anion-radical formed at the first stage was subject to very fast disproportionation with the formation of a dianion and the starting compound which was reduced again (Scheme 4).

The latter mechanism should be manifested in a formally two-electron wave in the CV curve, which was in line with the experiment. The disproportionation could be likely due to the instability of the anion-radical formed at the first stage. However, that fact somehow contradicted the reference data on the reduction of the



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compounds with quinoid structure [6], since it is known that such compounds are reduced via two sequential single-electron stages. Most of the reference data on the reduction of quinoid compounds have been reported for the only solvent, and thus the role of solvent on the stability of intermediate compounds cannot be elucidated. Yet this in an important issue, since the solvent nature is an extremely significant factor affecting the stability of mixed-valence compounds. Therefore, we planning to study electrochemical behavior of compounds **3a–3c** in other solvents.

Another possible factor enhancing the stability of anion-radicals formed at first stage is the introduction of acceptor substituents at the central ring. To investigate that, we studied the behavior of compounds **3b** and **3c**. CV of compound **3b** is given in Fig. 2. As in the case of compound **3a**, one reversible wave at E = 0.195 V was observed. In comparison with compound **3a**, the reduction potential was shifted towards positive values, in good accordance with the electronomer effect of the substituent. However, disproportionation of anion-radical formed at the first stage of reduction was not prevented by the introduction of a bromine atom. The increase in the potential scan rate to 1 V/s (Fig. 2) did not allow the detection of the anion-radical. Thus, electrochemical behavior of compound **3b** could be described by Scheme 4.

The introduction of the second bromine atom at the central phenyl ring qualitatively changed the electrochemical properties (Fig. 3): two reversible reduction peaks were observed, at E = 0.400 and E =0.275 V, even at low potential scan rates. In comparison with compounds 3a and 3b, the reduction potential was strongly shifted towards the anodic region. Such strong shift could not be explained exclusively by the electronic effects of an additional bromine atom, since the reduction potential of compound **3b** was only slightly shifted in comparison with compound 3a. Moreover, the second reduction potential of compound 3c was also more negative than the first potential of compounds 3a and 3b. That fact indicated that even anion-radical possessed higher accepting properties. It could be argued that compound **3c** formed a biradical specie in a solution, in which two radical centers did not interact (or the interaction was weak) and the reduction process occurred at those radical centers. That could be due to disruption

of the coplanarity of quinoid system of compound **3c** by the bromine atoms in positions 2 and 5.

Hence, electrochemical behavior of compound 3c could be expressed by Scheme 5. The reduction of compound 3c occurring at the first stage gave a stable anion-radical form. Since the introduction of two bromine atoms at the central ring strongly lowered the energy of HOMO at which reduction process was localized, the potentials were strongly shifted towards the anodic region. At the second stage, the anion-radical was reduced into dianion **A** which was stable over time and did not undergo any chemical transformations.

In summary, the obtained CV data suggested that compound **3c** was readily transformed into the biradical form in a solution. At the same time, it possessed strong accepting properties in neutral as well as in anionradical forms. That was due to the introduction of the substituents disrupting the coplanarity of the quinoid system of compound **3c** and favored localization of the radicals at the imidazole fragments. That in turn led to the biradical system formally exhibiting the properties of a monoradical system. Expectedly, the reduction potential of compound **3c** was strongly shifted to the anodic region. That fact coincided well with the reference data on the reduction of monoradical compounds.

## EXPERIMENTAL

The solvents were dried and distilled prior to the use. Commercial chemicals (Sigma-Aldrich) were used as received.

IR spectra were obtained using an InfraLYuM FT-02 Fourier spectrometer (KBr pellets). <sup>1</sup>H and <sup>13</sup>C NMR spectra were registered using a JNM-ECX400 Jeol spectrometer (400.1 and 100.6 MHz, respectively; solution in  $CDCl_3$  or  $DMSO-d_6$ . Chemical shifts were referenced to the residual signals of deuterated solvents. Elemental analysis was performed using a Vario MICRO CHNS-analyzer. The conditions of analytical TLC were as follows: sorbent - Silufol UV-245, eluent – methylene chloride–ethylacetate (2 : 1), development in iodine chamber. Column chromatography was performed using L40/100  $\mu$  silica gel, eluting with benzene. Electrochemical reduction potentials were measured in a 5 mL electrochemical cell using a Gamry digital potentiostat-galvanostat (Canada), connected to a personal computer. Voltammograms were registered with 0.05 M of *n*-Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>3</sub>CN as background electrolyte at 20°C in a special 10 mL electrochemical

cell. The oxygen was removed via bubbling with dry argon. Cyclic voltammetry experiment was performed at different scan rates using a standard platinum electrode ( $S = 0.6 \text{ cm}^2$ ) and saturated silver chloride reference electrode (potential vs Fc/Fc<sup>+</sup> –0.55 V in CH<sub>3</sub>CN). The determined potential values were recalculated with consideration of ohmic losses.

Terephthalaldehyde 1a, 2,5-dibromoterephthalaldehyde 1c [7], imidazoles 2a–2c, and quinones 3a–3c were synthesized as described elsewhere [8, 9]

**2-Bromoterephthalaldehyde (1b).** 8.5 mL (0.15 mol) of  $H_2SO_4$  was added to a mixture of 3.7 g (0.02 mol) of 2-bromoxylene, 60 mL (0.95 mol) of glacial acetic acid, and 56.5 mL (0.1 mol) of acetic anhydride at continuous cooling and stirring, maintaining the reaction mixture temperature at 6–12°C. 10 g (0.1 mol) of CrO<sub>3</sub> was added to the obtained reaction mixture in small portions maintaining the reaction mixture temperature at 5–10°C. After addition of CrO<sub>3</sub>, the stirring had been continued for 1.5 h at 6–12°C; then the reaction mixture for 24 h. The precipitate was filtered off, dried in air, and recrystallized from ethanol.

The mixture of 6.26 g (0.015 mol) of the acetoxy derivative, 60 mL of ethanol, 10 mL of water and 8 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was refluxed for 1.5 h, and then the reaction mixture was cooled to room temperature and diluted with water (200 mL). Light-yellow precipitate was filtered off and purified by recrystallization from a CHCl<sub>3</sub>–petroleum ether mixture. Yield 2.56 g (80.1%). IR spectrum, cm<sup>-1</sup>: 1696 s (C=O), 1199 m, 817 m, 694 m. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 7.72–7.81 m (2H), 8.15 d. d (1H, *J* = 1.8, 0.4 Hz), 10.33 s (1H), 10.37 s (1H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{C}$ , ppm: 125.3, 126.1, 130.5, 131.7, 135.4, 137.6, 189.5, 190.2 (C=O).

General procedure for the synthesis of compounds 2a–2c. A mixture of 0.7 mmol of aldehyde 1a–1c, 300 mg (1.4 mmol) of benzene, 700 mg (1.9 mmol) of ammonium acetate, and 20 mL of glacial acetic acid was refluxes for 2 h. The precipitate was dissolved during refluxing, and the solution color turned golden. Then the reaction mixture was cooled; 50 mL of water and 10 mL of ammonia solution were added. The precipitate was filtered off and dried in air. Fine-crystalline yellow powder was obtained.

1,4-Bis(4,5-diphenylimidazol-2-yl)-benzene (2a). Yield 270 mg (75%),  $bp > 300^{\circ}C$  (decomp.). IR spectrum,

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v, cm<sup>-1</sup>: 3375 m (NH), 1659 m (C=C<sub>Ar</sub>), 1509 s (C=C<sub>Ar</sub>), 1339 m (C=N), 1126 m, 895 s. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 12.92 br. s (NH, 2H), 7.29–7.52 m (12H), 7.62–7.71 m (8H), 8.07 d. d (4H, *J* = 8.7, 1.9 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 124.2, 126.9, 127.1, 128.6, 128.9, 130.4, 133.3, 137.7, 148.2. Found, %: C 84.05; H 5.07; N 10.86. C<sub>36</sub>H<sub>26</sub>N<sub>4</sub>. Calculated, %: C 84.02; H 5.09; N 10.89.

**1,4-Bis(4,5-diphenylimidazol-2-yl)-2-bromobenzene (2b).** Yield 350 mg (84%), bp > 300°C (decomp.). IR spectrum, v, cm<sup>-1</sup>: 3360 m (NH), 1662 m (C=C<sub>Ar</sub>), 1504 s (C=C<sub>Ar</sub>), 1343 m (C=N), 1130 m, 894 s, 698 s (C–Br). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 12.71 br. s (NH, 2H), 7.45–7.64 m (12H), 7.78 d. d (1H, J = 8.5, 1.9 Hz), 7.83–7.92 m (4H), 7.95–8.02 m (3H), 8.08 d. d (1H, J = 1.9, 0.4 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 122.7, 124.2, 126.3, 126.8, 126.9, 127.1, 127.8, 128.6, 129.0, 130.4, 130.7, 133.3, 137.7, 148.2. Found, %: C 72.66; H 4.24; N 9.46. C<sub>36</sub>H<sub>25</sub>BrN<sub>4</sub>. Calculated, %: C 72.85; H 4.25; N 9.44.

**1,4-Bis (4,5-dyhenylimidazol-2-yl)-2,5-dibrombenzene (2c)**. Yield 330 mg (70%), bp > 300°C (decomp.). IR spectrum, v, cm<sup>-1</sup>: 3325 m (NH), 1672 s (C=C<sub>Ar</sub>), 1594 m (C=C<sub>Ar</sub>), 1344 m (C=N), 1284 s, 694 s (C–Br). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 12.75 br. s (NH, 2H), 7.45–7.63 m (12H), 7.87 d. d. d (4H, *J* = 7.1, 2.0, 1.5 Hz), 7.93 d. d. d (4H, *J* = 7.7, 1.7, 1.5 Hz), 8.08 d (2H, *J* = 0.4 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 120.7, 124.2, 126.3, 126.9, 128.6, 128.9, 129.2, 130.4, 130.7, 133.3, 137.7, 148.2. Found, %: C 64.32; H 3.61; N 8.36. C<sub>36</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>4</sub>. Calculated, %: C 64.30; H 3.60; N 8.33.

General procedure for the synthesis of quinones **3a–3c.** 100 mL of 20% solution of  $K_3[Fe(CN)_6]$  was added to a mixture of 12.5 mL of 6% solution of KOH and a suspension of 1 mmol of compound 2a-2c in 25 mL of dioxane at continuous stirring during 2 h under argon atmosphere, maintaining temperature of the reaction mixture at 5-7°C. When first drops of the  $K_3[Fe(CN)_6]$  solution were added, the reaction mixture turned purple and then became green. After the addition of K<sub>3</sub>[Fe(CN)<sub>6</sub>], the reaction mixture was stirred under argon atmosphere at 5–7°C for 30 min; the precipitate was filtered off, washed with huge amount of water, and dried in air. Fine-crystalline purple precipitate was obtained. To remove the unreacted starting component, the product was dissolved in 50 mL of benzene and separated from the undissolved residue. The benzene solution was evaporated in vacuum to 10 mL volume, and 5 mL of octane was added. The precipitate was filtered off and dried in air. Fine-crystalline green powder was obtained.

**3,6-Bis(4,5-diphenylimidazol-2-yliden)-1,4cyclohexadiene (3a).** Yield 120 mg (25%), bp 135–137°C (benzene–octane). IR spectrum, v, cm<sup>-1</sup>: 1610 m (C=C<sub>Ar</sub>), 1571 m (C=C<sub>Ar</sub>), 1333 m (C=N), 1290 m, 895 s. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 6.95 d (4H, *J* = 10.2 Hz), 7.52–7.62 m (12H), 8.07 d. d. d (8H, *J* = 7.9, 1.7, 1.5 Hz). <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta_{C}$ , ppm: 107.1, 128.2, 129.1, 131.2, 132.1, 133.2, 134.9, 140.1, 159.8. Found, %: C 84.32; H 4.71; N 10.96. C<sub>36</sub>H<sub>24</sub>N<sub>4</sub>. Calculated, %: C 84.35; H 4.72; N 10.93.

**3,6-Bis(4,5-dyphenylimidazol-2-yliden2)-2-bromo-1,4-cyclohexadiene (3b).** Yield 140 mg (23.6%), bp 157– 158°C (benzene–octane). IR spectrum, v, cm<sup>-1</sup>: 1604 m (C=C<sub>Ar</sub>), 1566 m (C=C<sub>Ar</sub>), 1326 m (C=N), 1280 m, 894 s, 694 s (C–Br). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 7.51–7.58 m (4H), 7.58–7.68 m (8H), 7.78–7.85 m (4H), 7.93–8.04 m (2H), 8.12 s (1H), 8.20–8.26 m (4H). <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta_{\rm C}$ , ppm: 108.1, 114.2, 121.4, 127.2, 128.7, 128.9, 129.2, 132.2, 133.2, 134.9, 150.6, 158.9. Found, %: C 73.12; H 3.91; N 9.46. C<sub>36</sub>H<sub>23</sub>BrN<sub>4</sub>. Calculated, %: C 73.10; H 3.92; N 9.47.

**3,6-Bis(4,5-diphenylimidazol-2-yliden)2,5-dibromo-1,4-cyclohexadiene (3c).** Yield 270 mg (30.2%), bp 172– 174°C (benzene–octane). IR spectrum, v, cm<sup>-1</sup>: 1609 m (C=C<sub>Ar</sub>), 1570 m (C=C<sub>Ar</sub>), 1333 m (C=N), 1282 m, 896 s, 699 s (C–Br). <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 7.55–7.67 m (12H), 7.78–7.85 m (8H), 8.02 s (2H). <sup>13</sup>C NMR spectrum (DMSO- $d_6$ ),  $\delta_C$ , ppm: 115.2, 120.4, 128.2, 129.2, 129.8, 131.9, 133.0, 133.2, 158.9. Found, %: C 64.47; H 3.32; N 8.39. C<sub>36</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>4</sub>. Calculated: C 64.50; H 3.31; N 8.36.

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#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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