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Synthesis of Radicals Underlain by 1,3-Bis(4,5-diphenylimidazol-2-yl)benzene

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Abstract—A dimer of a monoradical was obtained proceeding from 1,3-bis(4,5-diphenylimidazol-2-yl)benzene and the rate constants were measured of the dissociation of dimers of 1,3-bis(4,5-diphenylimidazol-2-yl)benzene mono- and biradicals.

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Bisimidazoles and radicals based thereon up till now remain a poorly studied division of the chemistry of stable free radicals. The oxidation of 1,4-bis(4,5-diphenylimidazol-2-yl)benzene is known to yield a quinone [1–4], 1,4-bis(4,5-diphenylimidazol-2-ylidene) cyclohexa-2,5-diene, that according to the statement of Sakaino et al. [2] is partially converted into a biradical on heating. Similarly the oxidation of 1,4-bis(2,5-diphenylimidazol-4-yl)benzene also gives a quinoid system [5]. However when in the benzene ring that connects two imidazole rings the hydrogen atoms are replaced by fluorine the quinone formed by the oxidation of the bisimidazole can exist in the equilibrium with the biradical [6]. This was found at the oxidation of 1,4-bis-(4,5-diphenylimidazol-2-yl)-2,3,5,6-tetrafluorobenzene. Thus obtained greenish-blue quinone on the crystallization from benzene gave a colorless dimer, and this would be possible only at the formation of a biradical [6]. The formation of quinoid systems is common for compounds where two imidazole rings are in the conjugation, and the connecting central ring may be a benzene as well as a five-membered heterocycle [4].

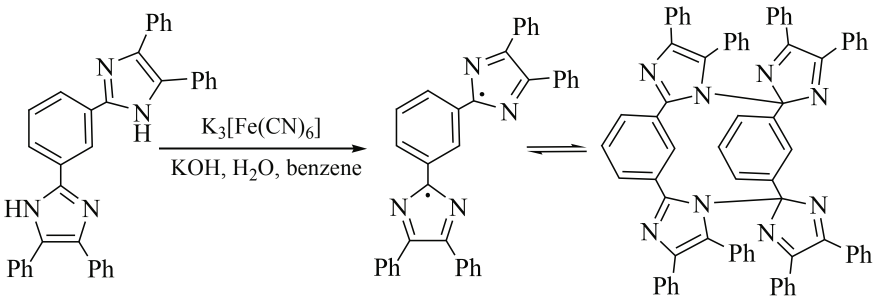
However when the two imidazole rings are not conjugated it is possible to obtain both mono- and biradical system depending on the conditions of the imidazole oxidation. This can be demonstrated by an example of 1,3-bis(4,5-diphenylimidazol-2-yl)benzene (**I**) [7].

In keeping with the previously advanced hypothesis connecting the relative stability of a radical and its existence in the solution with the solvating ability of the given solvent [8] it is presumable that if the oxidation would be carried out in a solvent where the formed radical is more soluble than the initial imidazole the oxidation would result in the bisimidazolyl radical. For instance, the oxidation of 1,3-bis(4,5-diphenylimidazol-2-yl)benzene (**I**) with potassium ferricyanide in the alkaline medium in the two-phase system benzene–water provided the corresponding biradical **II** isolated and characterized in the form of a dimer **IIa** [9]. The colored biradical **II** formed by the oxidation of imidazole **I** is unstable and becomes colorless giving dimer already in the course of its formation.

If the formed radical is less soluble under the reaction conditions than initial imidazole **I** the oxidation of a single imidazole ring should result in the formation of monoradical **III** insoluble under the given conditions that would not suffer oxidation at the second imidazole ring.

To prove this assumption we synthesized monoradical **III** by the oxidation of bisimidazole **I** [7] in the alkaline water-alcohol solution of potassium ferricyanide. The formed in the course of oxidation monoradical **III** precipitated in the form of the so-called “piezochromic dimer” **IIIa** [10, 11] with the appearance of a fine crystalline violet powder whose color was due to the presence of free imidazolyl radicals **III**. On dissolving

Scheme 1.



I **II** **IIa**

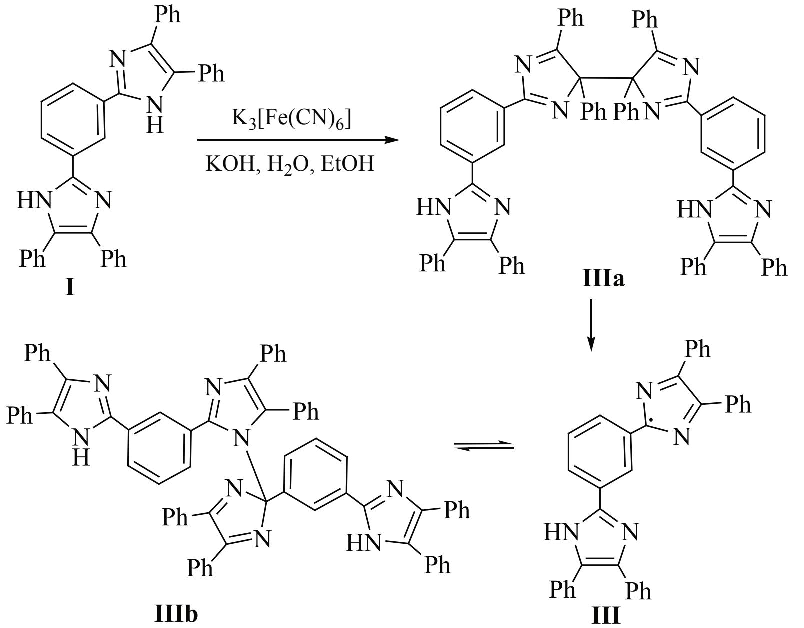
the “piezochromic dimer” **IIIa** in benzene the solution got crimson and quickly lost the color originating from the dissociation of dimer **IIIa** into radicals **III** followed by their dimerization into a “photochromic dimer**”** **IIIb** which was isolated in the crystalline form on evaporation of the benzene solution (Scheme 2). “Piezochromic dimer” is the product of the dimerization of imidazolyl radicals by the atoms with the highest density of the unpaired electron. The “photochromic dimer**”** originates from the donor-acceptor dimerization [8].

The structures of dimers **IIIa, IIIb** we suggest by the analogy to the structure of “piezochromic” and “photochromic” dimers of triphenylimidazolyl [11, 12] and the XRD data for “photochromic” dimer of 4,5-diphenyl-2-*o*-chlorohenylimidazolyl [13, 14]. The structure of “photochromic” dimer **IIa** was established earlier [9].

Dimer **IIIb** is light-green (λ_{max} 301 nm) and gives a weak singlet ESR signal both in solid state and in benzene solution thus showing the presence of a small concentration of nondimerized radicals **III**. It is likely to be due to the spatial hindrances arising at the formation of the corresponding dimers.

The formation of dimer **IIIb** was proved by its mass spectrum, and the structure suggested basing on the data of [9, 11–14] was confirmed by ^{13}C NMR spectrum where alongside with the signals characteristic of carbon atoms of the benzene and imidazole rings signals appeared at 112.25 ppm belonging to atom C^2 of 2*H*-imidazole ring

Scheme 1.



I **IIIa** **IIIb** **III**

Thermodynamic parameters of dissociation in toluene of radical dimers obtained from 1,3-*bis*(4,5-diphenylimidazol-2-yl)benzene

Dimer nature	Rate constants of dissociation $k \times 10^5$ s^{-1}							E_a, kJ mol^{-1}	log *A*	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
	55°C	60°C	65°C	70°C	75°C	80°C	85°C			70°C	
Dimer of monoradical **IIIb**	–	9.5	–	13.8	15.2	16.8	–	28.1	0.40	25.3	238.4
Dimer of biradical **IIa**	3.5	4.2	–	9.5	–	–	–	64.4	5.77	61.5	135.7
Dimer of 2,4,5-triphenyl-imidazolyl	–	–	19.7	35.0	60.3	–	133.3	95.9	11.13	93.0	32.9

existing in the sp^3–hybridization, and at 166.89 ppm characteristic of C^2 atom of the imidazole ring linked to the benzene ring [9].

In order to estimate the effect of the structure of dimers **IIa** and **IIIb** on the rate of their dissociation into radicals we studied the kinetics of this process by the method of radical traps using diphenylpicrylhydrazine (DPPH-H) [15] (see the table).

As seen from the table, the rate constants of the dissociation of dimers **IIa** and **IIIb** as well as the activation energies and the pre-exponential factors are significantly smaller than the corresponding values for the dimer of 2,4,5-triphenylimidazolyl [16]. This may be due only to considerable steric hindrances from the presence of two imidazole rings in the *meta*-position of the central benzene ring distorting the planarity of the system of the dimer molecule as is confirmed by the XRD data for dimer **IIa**: The imidazole rings are turned with respect to the central benzene ring by 82–83 deg [9].

To estimate the role of the steric factors and their effect on the dissociation rate of dimers **IIa** and **IIIb** thermodynamic parameters of this process at 70°C were calculated. As seen from the table, the $\Delta S^{\neq}$ values indicate the governing influence of the steric factors on the dissociation rate of the dimers. At the same time the steric factor is more important for dimer **IIIb** than for dimer **IIa** and triphenylimidazolyl dimer.

EXPERIMENTAL

The reaction products were analyzed by TLC on Silufol UV-254 plates (eluents petroleum ether, acetone, dichloromethane), development in iodine vapor under UV irradiation IR spectra were recorded on a spectrophotometer Infra-Lyum FT-02 from pellets with KBr. UV spectra in visible region were taken on spectrophotometers Specord UV vis and SF-16. ESR spectra were registered on an instrument EPA 2M. Mass spectra MALDI-TOF of positive ions were obtained on an instrument Bruker Autoflex (UV laser, 336 nm). The samples were placed on a nickel plate, matrix was 2,5-dihydroxybenzoic acid. ^{13}C NMR spectrum was registered on a spectrometer Bruker AMX-400 (100 MHz) in DMSO-d_6.

1,3-Bis(4,5-diphenyl-1*H*-imidazol-2-yl)benzene (**I**) and dimer 2,2'-(*m*-phenylene)bis(4,5-diphenylimidazol-1-yl)biradical (**IIa**) were obtained by procedures [7, 9] respectively.

2,2'-Bis[3-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenyl]-4,4',5,5'-tetraphenyl-4*H*,4'*H*-4,4'-bisimidazol ("piezochromic" dimer of monoradical) (IIIa). To a solution of 0.5 g (1 mmol) of bisimidazole **I** and 0.6 g (1.5 mmol) of sodium hydroxide in 50 ml of ethanol at constant stirring was added dropwise a solution of 1 g (3 mmol) of potassium ferricyanide in 100 ml of water within 1 h at 5–10°C. Then the reaction mixture was stirred for 0.5 h at room temperature. The separated light-violet fine crystalline precipitate was filtered off and washed on the filter with water till neutral washings. The product was dried in air. Yield 0.3 g (60%). Light-violet crystals, mp 203–205°C. IR spectrum, ν, cm^{-1}: 3630 (NH), 1604 (imidazole), 1550, 1535, 1527, 1512 (4*H*-imidazole).

2-[3-(1-{2-[3-(4,5-Diphenyl-1*H*-imidazol-2-yl)-phenyl]-4,5-diphenyl-2*H*-imidazol-2-yl}-4,5-diphenyl-1*H*-imidazol-2-yl]phenyl)-4,5-diphenyl-1*H*-imidazol ("photochromic" dimer of monoradical) (IIIb). A solution of 0.51 g (0.5 mmol) of «piezochromic» dimer of monoradical **IIIa** in 25 ml of benzene was evaporated in a vacuum to the volume of 10 ml. The separated gray-green precipitate was filtered off and dried in air. Yield 0.5 g (100%). Gray-green crystals, mp 212–214°C. IR spectrum, ν, cm^{-1}: 3406 (NH), 1604 (2H-isoimidazole), 1558, 1500 (C^2–N^1 of imidazoles). ^{13}C NMR spectrum, δ, ppm: 112.25, 122.58, 125.18, 126.67, 126.77, 127.22, 127.43, 128.40, 128.82, 129.21, 129.71, 131.12, 131.94, 134.38, 135.39, 137.38, 137.54, 138.14, 138.58, 145.08, 145.32, 145.58, 148.06, 148.46, 166.89. Mass spectrum: *m/z* 1027. Found, %: C 84.41; H 5.02; N 10.31. $C_{36}H_{25}N_4$. Calculated, %: C 84.07; H 4.81; N 10.89. *M* 1027.22.

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