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Synthesis, Structure, and Spectral Luminescent Properties of Novel 1,2,4-Triazole Derivatives Containing Benzthiazole Group

A. D. Beldovskaya[a], G. A. Dushenko[b,c], N. I. Vikrishchuk[d], L. D. Popov[d], Yu. V. Revinskii[b], and I. E. Mikhailov[b,d]

[a] *Institute of Arid Zones, Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*
[b] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*
[c] *Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*
[d] *Southern Federal University, ul. Zorge 7, Rostov-on-Don, 344090 Russia*
e-mail: natvi2004@mail.ru

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Abstract—Novel derivatives of 1,2,4-triazol with benzthiazole fragment have been prepared, including Cu(II) and Be complexes. Their structure and spectral luminescent properties have been investigated. With *o*-hydroxyphenylbenzthiazolyl-1,2,4-triazole as an example, the density functional theory has been applied to find the stable conformers with different structures of coordination nodes, stabilized by intramolecular hydrogen bonds between hydroxyl group hydrogen and either triazole of benzthiazole nitrogen.

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The recently emerged interest to 1,2,4-triazoles and their derivatives is mainly due to their various biological activity [1–4] and excellent complexing ability [5, 6]. The most remarkable complex formation properties are revealed by *o*-hydroxyphenyltriazoles containing =N(O)-phenol chelating node [7–11]; based on them, a series of metal complexes with important utilitarian properties has been prepared and characterized [12–17]. Furthermore, being efficient and photostable organic luminophors generating ultraviolet and short-wavelength visible light, triphenyltriazoles have been applied as elements of active laser media [18], efficient electron transport materials in organic light-emitting diodes (OLEDs) [19–21], and highly selective fluorescent chemosensors for metal cations [22, 23].

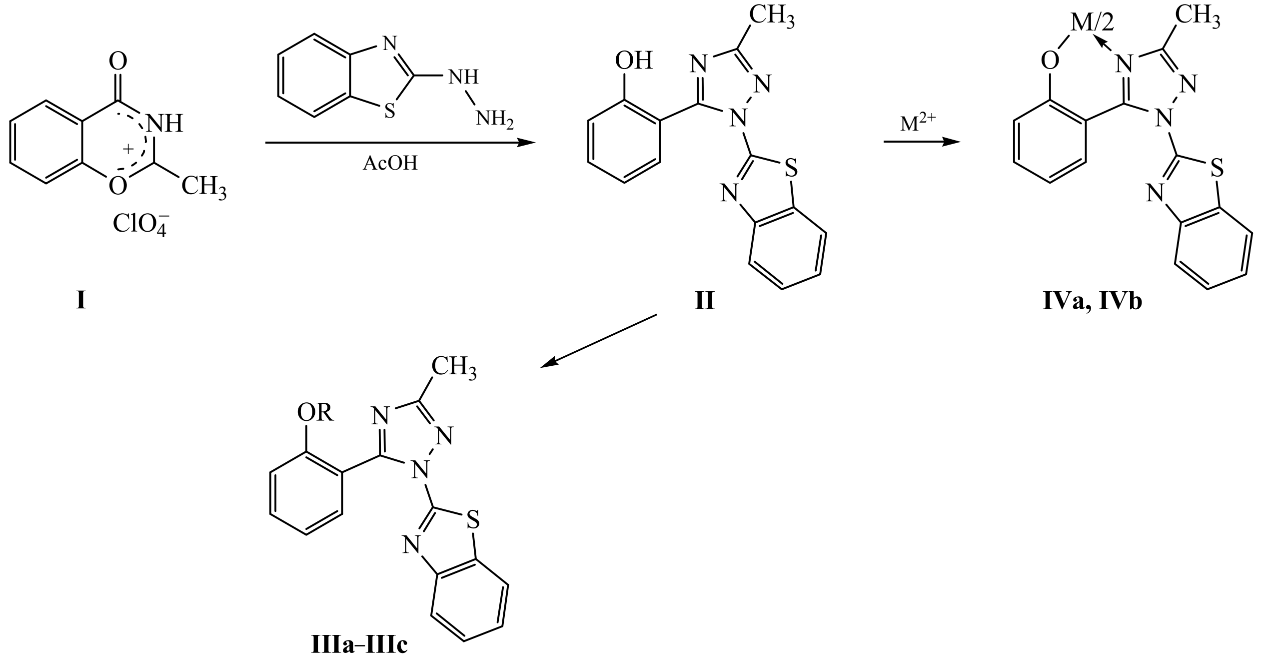
This work aimed to prepare novel derivatives of 1,2,4-triazole containing benzthiazole fragment, including their metal complexes, and to elucidate their structure as well as their spectral luminescent properties, important for OLED applications. Moreover, as 5-(2'-hydroxyphenyl)-3-methyl-1-benzthiazolyl-1,2,4-triazole **II** and its derivatives contain the pharmacophore benzthiazole and 1,2,4-triazole groups, the prepared products will further extend the variety of biologically active compounds of this class.

o-Hydroxyphenyl-1,2,4-triazole **II** and its derivatives (**IIIa**–**IIIc**, **IVa**, and **IVb**) were prepared using 4-oxo-1,3-benzoxazinium perchlorate **I** [24].

In particular, 5-(2'-hydroxyphenyl)-3-methyl-1-benzthiazolyl-1,2,4-triazole **II** was obtained via recyclization of the product of reaction between **I** and benzthiazolylhydrazine; subsequent methylation of **II** with methyl iodide in the presence of silver oxide gave methyl ether (**IIIa**); treatment of **II** with acetic anhydride in the presence of catalytic amounts of 70% perchloric acid led to the acetate (**IIIb**); finally, reaction of **II** with tosyl chloride and anhydrous potassium carbonate in butanone resulted in the tosylate (**IIIc**).

Structure of all the newly prepared compounds was confirmed by elemental analysis, ^{1}H NMR, ^{13}C NMR, UV, IR, MS, quantum-chemical methods, and electronic and fluorescent spectroscopy.

In the IR spectra of **IIIa**–**IIIc**, **IVa**, and **IVb**, the stretching vibration bands of C=N and C=C were observed at 1436–1620 cm^{-1}. All those compounds (including the ligand **II**) contained three different types of C=N bonds: two in the triazole ring and one in the benzthiazole fragment. Upon formation of the



R = Me (**IIIa**), Ac (**IIIb**), Ts (**IIIc**); M = Be (**IVa**), Cu (**IVb**).

complexes **IVa** and **IVb**, the band of C^5=N^4 stretching was shifted to lower frequencies by 24–30 cm^{-1} (to 1563–1575 cm^{-1}) as compared with the corresponding band in the triazoles **II** and **IIIa–IIIc** spectra (1593–1599 cm^{-1}), whereas IR properties of the two other C=N bonds were less sensitive to complex formation. Formation of **IIIa–IIIc**, **IVa**, and **IVb** from triazole **II** was accompanied with vanishing of the OH group band at 3120 cm^{-1} (II) [11]. IR spectrum of the acyl derivative **IIIb** revealed the intense bands at 1742 and 1764 cm^{-1} (C=O), evidently, due to pair of acyl conformers; the spectrum of tosyl derivative **IIIc** contained SO_2 vibration bands at 1168 and 1368 cm^{-1}.

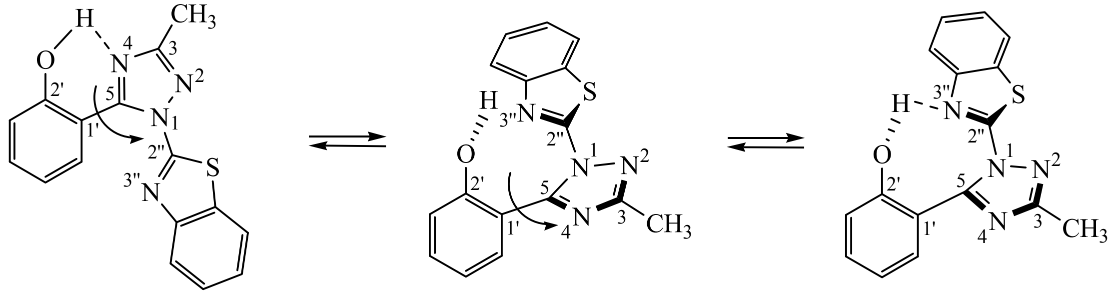
In the ^{1}H NMR spectra of **IIIa–IIIc** and **IVa** in $CDCl_3$, the signal of methyl group of triazole fragment was observed at 2.09–2.53 ppm, whereas the aromatic protons resonated at 6.52–8.16 ppm. The ^{13}C NMR spectra of triazoles **IIIa–IIIc**, contained 17 (**IIIa**), 18 (**IIIb**), and 21 (**IIIc**) carbon signals, including 7, 8 and 9 “quaternary” ^{13}C signals, respectively, and were in full accordance with the assumed structures. In the monoresonance ^{13}C spectra of the same compounds: the “quaternary” C^5 of triazole ring signal was observed as doublet [150.67 ppm and $^3J_{C,H}$ 4.4 Hz (**IIIa**), 152.50 ppm and $^3J_{CH}$ 5.0 Hz (**IIIb**), and 151.20 ppm and $^3J_{C,H}$ 3.7 Hz (**IIIc**)] due to far spin-spin interaction with $H^{3'}$ of the phenolic fragment; the signal of C^3 in triazole ring appeared as quartet [165.46 ppm and $^2J_{C,H}$ 7.5 Hz (**IIIa**), 162.57 ppm and $^2J_{C,H}$ 7.5 Hz (**IIIb**), and 162.13 ppm and $^2J_{CH}$ 6.9 Hz (**IIIc**)] due to far spin-spin interaction with protons of methyl group at C^3; the signal of $C^{2''}$ in thiazole ring was singlet at 135.86 ppm (**IIIa**), 156.90 ppm (**IIIb**), and 156.81 ppm (**IIIc**), as $^4J_{C,H}$ far spin-spin interaction with aromatic protons was not observed. The mentioned spectral features of **IIIa–IIIc** coincided with the monoresonance ^{13}C spectra of **II** [11].

Mass spectra of **IIIa–IIIc** contained the molecular ion peak and the peaks of the secondary ions, products of the molecular ion decay. The fragmentation of **IIIa–IIIc** molecular ions occurred majorly via simultaneous splitting of N^4–C^3 and C^5–N^1 or of N^4–C^3 and N^1–N^2 of the triazole ring, and subsequent decay into low molecular weight ions. In the electrospray ionization (ESI) mass spectra of the complexes **IVa** and **IVb**, besides the molecular ion peak, the peaks assigned to ion-molecular associates with sodium cation and to the fragments formed due to elimination of one of the ligands were registered.

Triazoles **II** and **IIIa–IIIc** were conformationally non-rigid due to free rotation of the phenol and benzthiazole fragments around their single bonds with the triazole ring; that could lead to formation of different coordination nodes and, therefore, to different complexes structure.

In order to deeper investigate the conformational possibilities, for triazole **II** taken as a representative example, by means of the DFT B3LYP/6-31G(d,p) method we estimated the relative stability of the isomeric and conformational forms with varied structure of the coordination nodes; further, we estimated the energy barriers of their transitions via rotation around the single bond between hydroxyphenyl and triazole rings, as well as of the hydroxyl rotation around the C–O bond.

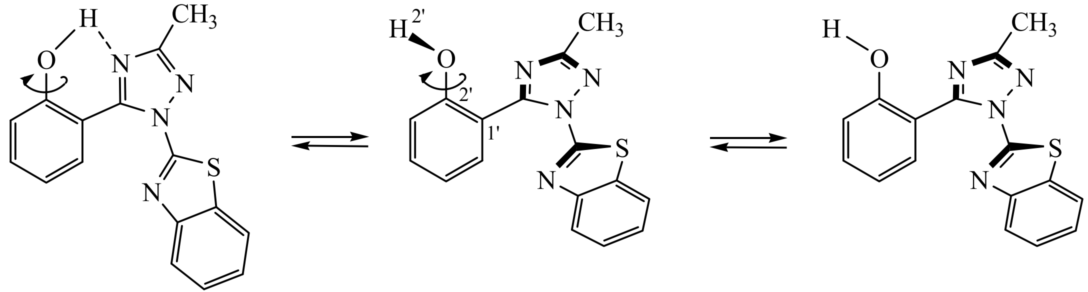
According to the gas phase computations, the structures **IIa**–**IId** corresponded to the minima at the potential energy surface of **II**.



IIa **IIe** **IIb**

The rotamers **IIa** and **IIb** (formed by rotation of the phenol and triazole rings around $C^{1'}$–C^{5}) were similar in stability (ΔE_{ZPE} 3.0 kcal mol^{-1}), the **IIa** form corresponding to the global minimum of the potential energy surface. The barrier $\Delta E^{\neq}_{\text{ZPE}}$ of the **IIa**→**IIb** transition via the intermediate state **IIe** was of 8.0 kcal mol^{-1} (Figs. 1 and 2, Table 1), that was consistent with the presence of both rotamers with the six-membered (**IIa**) and eight-membered (**IIb**) coordination nodes, being in equilibrium due to fast rotation around $C^{1'}$–C^{5} In **IIe**, the rings were almost orthogonal, the $C^{2'}C^{1'}C^{5}N^{4}$ torsion angle was of 96.1° .

According to the computations, the rotamer **IIc** with the hydroxyl in *exo* position was less stable than **IIa**, by ΔE_{ZPE} = 8.9 kcal mol^{-1}.

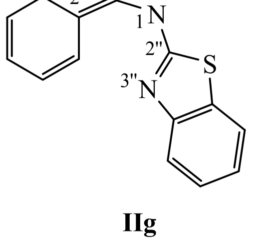


IIa **IIf** **IIc**

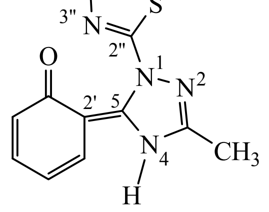
The energy barrier of the (**IIa**)→(**IIc**) transition via rotation around the C–O bond, through the **IIf** intermediate was of 10.6 kcal mol^{-1} (Fig. 3, Table 1). In the intermediate **IIf**, the hydroxyl group was off the phenyl ring plane (torsion angle $C^{1'}C^{2'}OH^{2'}$ of 113.4°).

Significant difference in thermodynamic stability between **IIa** and **IIb** pair as compared with **IIc** was due to formation of the stabilizing intramolecular hydrogen bonds in **IIa** and **IIb** (Fig. 1). The calculated energy barrier of rotation around C–O (10.6 kcal mol^{-1}), unexpectedly high for such process, was as well due to stabilization of **IIa** by the hydrogen bonding between hydroxyl hydrogen atom and the triazole nitrogen.

The latter reason should have resulted in the possibility of hydrogen transfer from phenolic oxygen to triazole nitrogen in **IIa** with formation of the isomer **IIg**. However, according to the computations, **IIg** was



IIg



IId

Table 1. Total and relative energy of the ground state structures of conformers and isomers of **II** in gas phase, and of their intermediates [B3LYP/6-31G(d,p)[a]]

Comp. no.	E_{total}, au	ΔE_{ZPE}, kcal mol^{-1}	ω_1, cm^{-1}
IIa	–1309.3860	0[b]	19
IIb	–1309.3808	3.0	29
IIc	–1309.3708	8.9	20
IId	–1309.3378	29.5	28
IIe	–1309.3721	8.0	–39[c]
IIf	–1309.3673	10.6	–370[c]

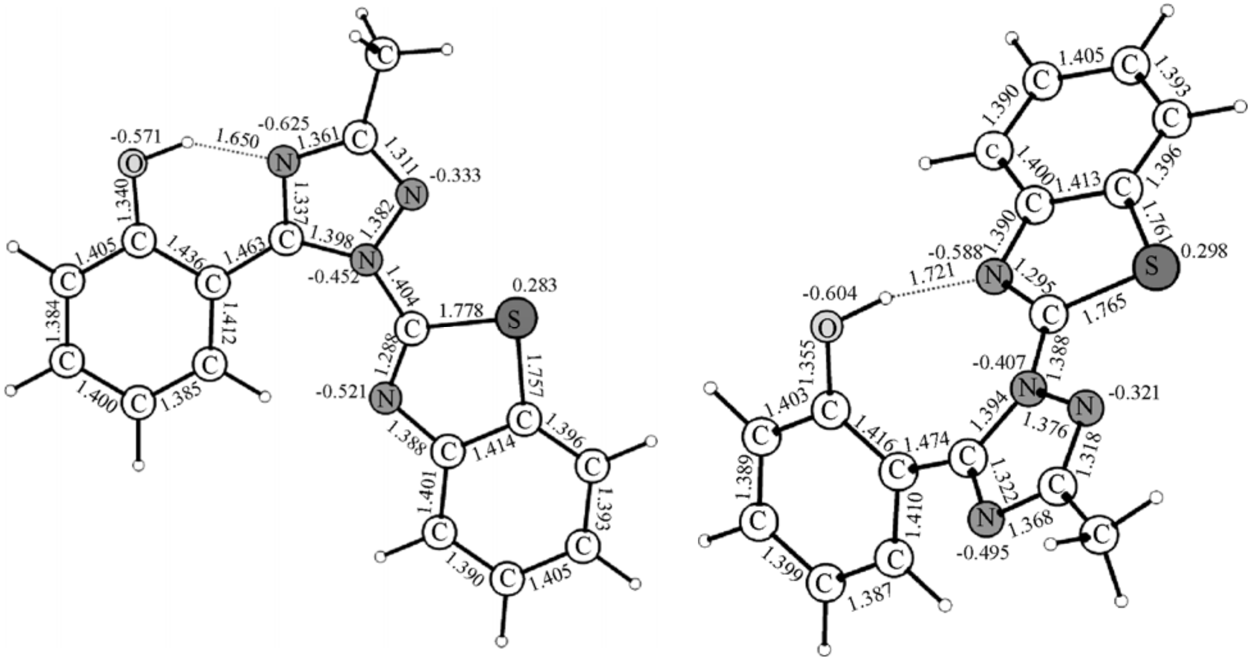
[a] E_{total} is total energy, 1 au = 627.5095 kcal/mol; ΔE_{ZPE} is relative energy accounting for zero harmonic oscillations; ω_1 is the lowest harmonic oscillation frequency. [b] E_{ZPE} (**IIa**) = –1309.1305 au. [c] The only imaginary harmonic oscillation frequency.

unstable and was not located at the potential energy surface of **II**. The keto form **IId** was localized in a local minimum, the corresponding structure had the benzthiazolyltriazole fragment rotated by 180°, that fragment was non-planar (torsion angle $C^5N^1C^{2''}N^{3''}$ of –42.7°). The **IId** isomer was less stable that **IIa** by ΔE_{ZPE} = 29.5 kcal mol^{-1} (Table 1); thus, the hydrogen transfer in the ground state was impossible.

However, formation of the quinoid isomer **IId** could be realized by the photoinitiated excited state intramolecular proton transfer (ESIPT) from the phenol group to the nitrogen atom of the triazole ring. The possibility of ESIPT process in the case of **II** was due to considerable increase of acidity of the phenolic hydroxyl and the basicity of the imine nitrogen in the triazole fragment upon excitation. That was observed in the case of *o*-hydroxyphenylazoles [18, 25], structurally similar to **II**.

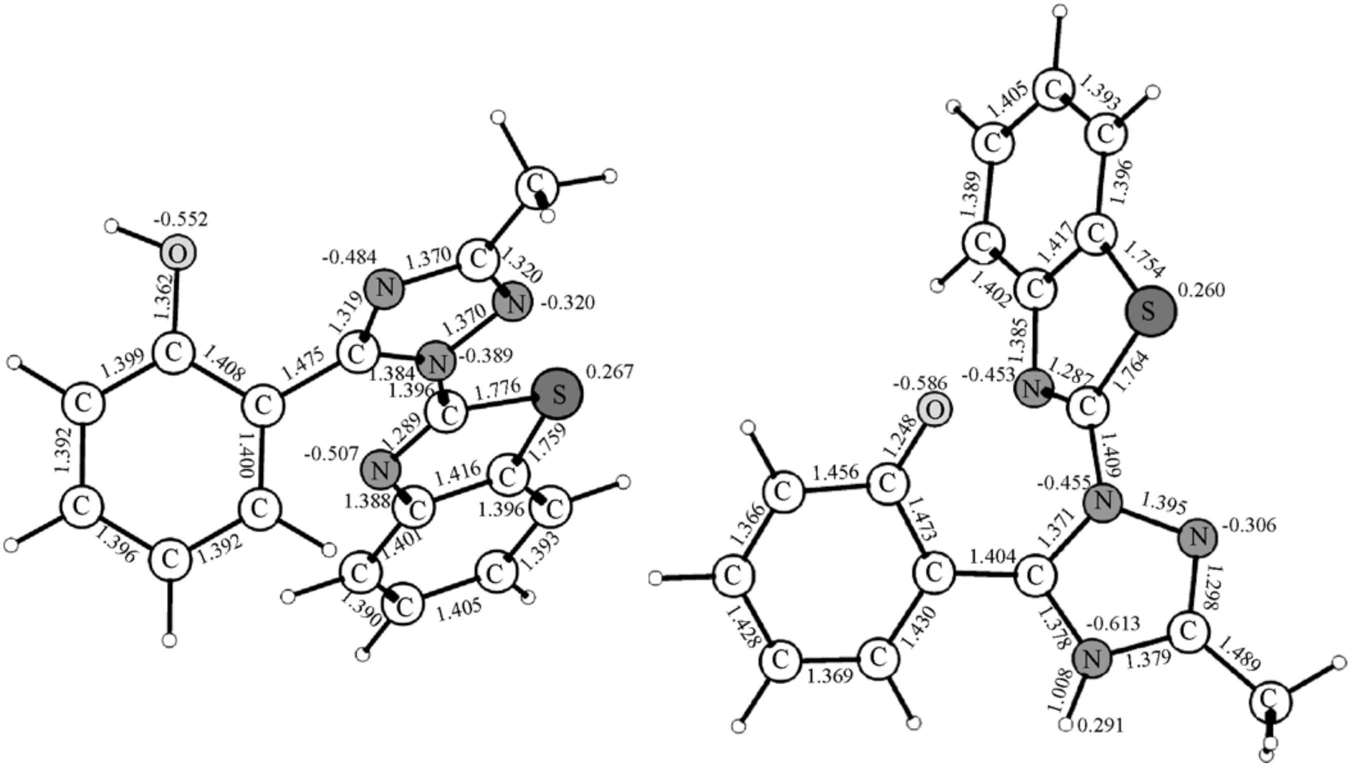
In the electronic absorption spectrum of **II**, the absorption maximum of the long-wavelength band due to $\pi \rightarrow \pi^*$ transitions was observed at 286–314 nm in polar (acetonitrile, DMSO) as well as in nonpolar (hexane, toluene) solvents (Table 2, Fig. 4), thus proving the existence of the benzoic structure **IIa** in the solutions.

In contrast to the absorption spectra, the spectra of luminescence of solutions of **II** were different depending on the solvent. In particular, in the polar solvents **II** revealed the luminescence at short wavelength: $\lambda_{\max}^{f\,1}$ = 334 nm (DMSO) or 392 nm (CH_3CN). In the nonpolar solvents the fluorescence



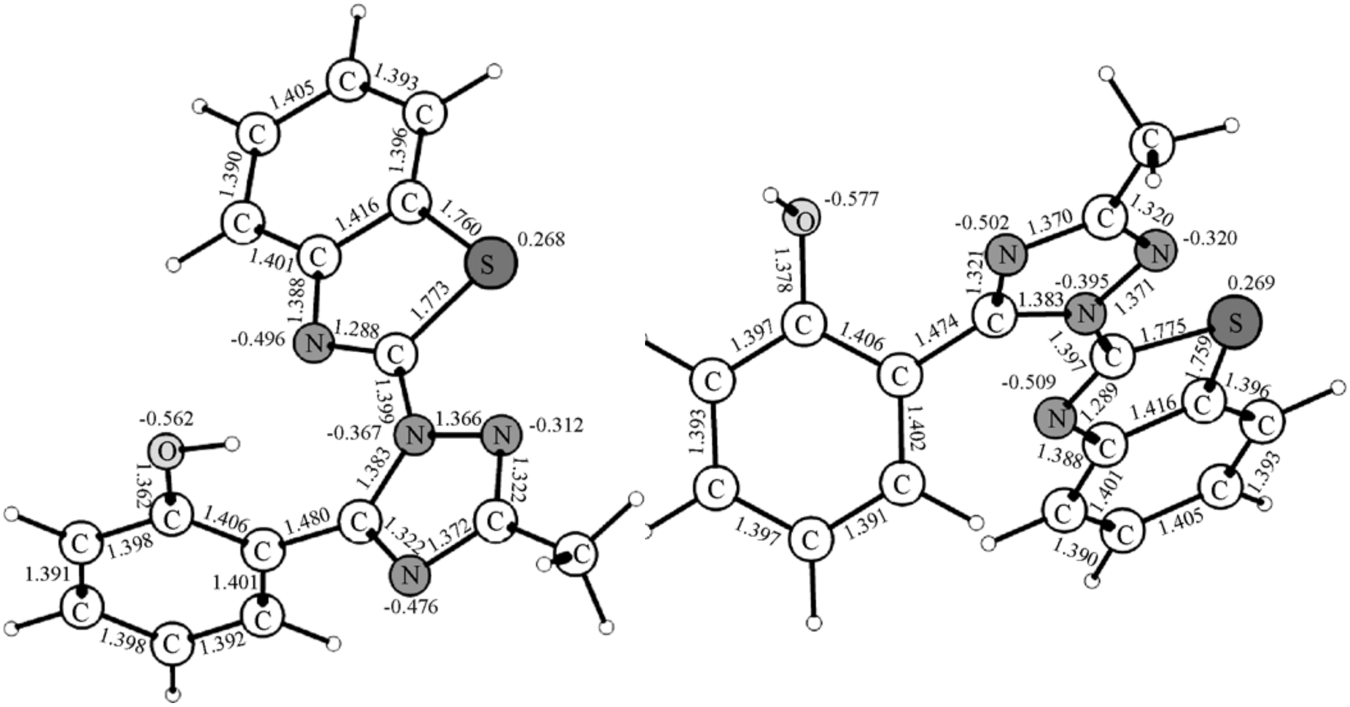
IIa, C_1 **IIb**, C_1

Fig. 1. Geometry parameters of **IIa** and **IIb** in gas phase and charges at atoms as computed by B3LYP/6-31G(d,p). Hereafter bond lengths are reported in Å.



IIc, C_1 **IId**, C_1

Fig. 2. Geometry parameters of **IIc** and **IId** in gas phase and charges at atoms as computed by B3LYP/6-31G(d,p).



IIe, C_1 **IIf**, C_1

Fig. 3. Geometry parameters and charges of rotation intermediates **IIe** and **IIf** in gas phase as computed by B3LYP/6-31G(d,p).

Table 2. Parameters of spectra of absorbance and fluorescence of **II**–**IV**[a]

Comp. no.	λ_{max}, nm ($\varepsilon \times 10^{-4}$, L mol^{-1} cm^{-1})			λ^{fl}_{max}, nm (φ)		
	toluene	acetonitrile	DMSO	toluene	acetonitrile	DMSO
II[b]	314 (1.62)	296 (1.27)	286 (1.57)	535 (<0.001)	392 (0.008)	334 (0.011)
IIIa	308 (1.71)	300 (1.32)	278 (1.21)	388 (<0.001)	353 (0.009)	337 (0.013)
IIIb	288 (1.18)	287 (1.25)	289 (1.45)	375 (0.008)	395 (0.011)	396 (0.028)
IIIc	297 (1.26)	294 (1.32)	296 (1.35)	390 (0.025)	398 (0.017)	408 (0.016)
IVa	368 (1.40)	356 (1.74)	359 (1.66)	457 (0.12)	460 (0.31)	465 (0.22)
IVb[c]	–	–	388 (1.57)	–	–	446 (0.005)

[a] Fluorescence at λ_{ex} = 300 nm. [b] In hexane, λ_{max} = 311 nm (1.34), λ^{fl}_{max} = 540 nm (0.003). [c] **IVb** was only soluble in DMSO.

was observed at λ^{fl}_{max} = 535 nm (toluene) or 540 nm (hexane), with unusually high Stokes shift of 13155–13635 cm^{-1}. The excitation spectra of **II** in the polar solvents were identical to the respective absorption spectra; therefore the observed luminescence was due to the benzoid form **IIa**, whereas in the nonpolar solvents the absorption and the excitation spectra were dissimilar. That the only form present in the solutions without irradiation was **IIa**, was confirmed by ^{1}H NMR spectrum in $CDCl_3$: the sharp signal at 11.39 ppm was observed, assigned to OH of phenolic fragment, whereas NH signal of **IId** form should have been found at 6–7 ppm. Furthermore, the very sharp form of the signal also pointed at the only rotamer in the solution. In the nonpolar solvents, the benzoid form **IIa** was stabilized by strong intramolecular hydrogen bond between phenolic hydroxyl and the triazole ring; that favored the proton transfer to the triazole nitrogen atom in the excited state via the ESIPT process, and led to formation of the quinoid **IId** structure, emitting in the long-wavelength region. In the polar solvents (or in the presence of water traces in the nonpolar solvents), the intermolecular hydrogen bond of triazole nitrogen and the solvent (or water) was formed instead, inhibiting the ESIPT process, thus only the short-wavelength emission of the **IIa** form was observed. The validity of that explanation was directly confirmed by addition of small amounts of DMSO to the toluene solution of **II**, accompanied by the appearance of the short-wavelength band in the emission spectrum. With more of the polar DMSO added, the intensity of that band steadily increased, whereas the long-wavelength emission was decreased (Fig. 5).

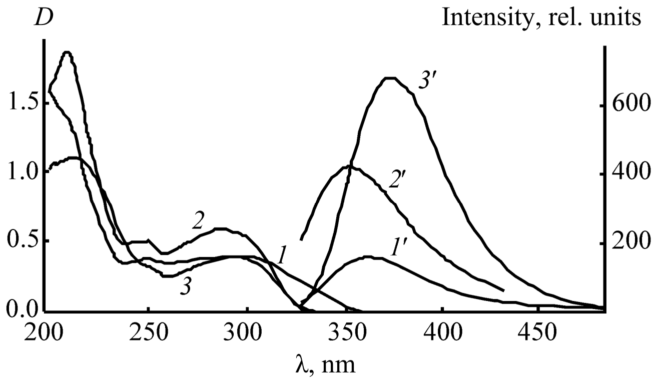


Fig. 4. Absorption (*1*–*3*) and fluorescence (*1'*–*3'*) spectra of **II** (*1* and *1'*), **IIIb** (*2* and *2'*), and **IIIc** (*3* and *3'*) in acetonitrile (c 2×10^{-5} mol/L).

The low quantum yield of triazole **II** luminescence (φ = 0.001–0.011, Table 2) was evidently due to radiationless deactivation of its excited state via the ESIPT mechanism. The absorption and luminescent properties of triazoles **IIIa**–**IIIc** with the fixed benzoic structure were in agreement with those of **II**, and confirmed the occurrence of the ESIPT process. In particular, the absorption spectra of **IIIa**–**IIIc** (λ_{max} = 288–297 nm, Table 1) were similar to that of **II**. In the emission spectra, independently of the solvent nature, only the short-wavelength luminescence was observed (λ^{fl}_{max} = 375–409 nm, Table 1) with ordinary Stokes shift values (5004–9274 cm–1). The ESIPT process in **IIIa**–**IIIc** was impossible due to the absence of mobile protons; therefore, the long-wavelength luminescence of **II** could be definitely assigned to the formation of quinoid structure **IId** in the excited state.

In contrast with the conformationally labile triazoles **II** and **IIIa**–**IIIc** showing low quantum yield of fluorescence, the corresponding Be complex **IVa** (L_2Be) revealed intense luminescence (φ 0.12–0.31) in the blue spectral region (λ^{fl}_{max} = 457–465 nm) (Fig. 2, Table 1), due to rigid tetrahedral configuration preventing the radiationless deactivation of the excited state. Thus, **IVa** was an efficient metal complex luminophor, promising for application in OLEDs.

Even though the absorption of the copper(II) complex **IVb** exhibited red shift by approximately 30 nm as compared with **IVa**, it revealed luminescence at the shorter wavelengths ($\lambda_{\max}^{\mathrm{fl}}$ = 446 nm) (Fig. 2, Table 2). The low quantum yield of luminescence in the case of **IVb** (φ = 0.005) was due to its paramagnetic properties, as evidenced by its effective magnetic moment at 298 K ($\mu_{\mathrm{ef}} = 2.21\mu_{\mathrm{B}}$, $\mu_{\mathrm{B}} = 927.4009\times10^{-26}$ J T^{-1}), and the broadened intense EPR signal ($g_{\|}$ = 2.073, $g_{\perp}$ = 2.019).

EXPERIMENTAL

IR spectra were recorded with Varian Excalibur 3100 FT-IR spectrometer in thin layer. ^{1}H NMR (250.13 MHz) and ^{13}C NMR (62.90 MHz) spectra in $CDCl_3$ were registered with Bruker DPX-250 spectrometer. The chloroform signals (δ_{H} 7.27 ppm and δ_{C} 77.00 ppm) were used as internal standard. The EPR spectrum of copper(II) complex **IVb** was registered in the solid state with Bruker EMXplus-10/12 spectrometer. Mass spectra were registered with Finnigan MAT INCOS 50 unit (direct injection) or with Finnigan LCQ Deca XP MAX unit (electrospray ionization, ESI). Absorption spectra were recorded with Cary Scan 100 spectrophotometer. Fluorescence spectra were recorded with Cary Eclipse spectrofluorimeter. All spectral measurements were performed at room temperature. The quantum yield of fluorescence was determined with respect to acetonitrile solution of anthracene according to

$$\varphi = \varphi_0 I D_0 / I_0 D n^2 / n_0^2,$$

where φ and φ_0, quantum yields of the studied sample fluorescence and of acetonitrile solution of anthracene, respectively; I and I_0, the integral intensities of the respective fluorescence spectra; D and D_0, respective absorbance at the excitation wavelength; n and n_0 refractive indices of the respective solutions. The quadratic term accounting for the refractive index difference was discussed in [25, 26]. The quantum yields were measured in dilute solutions, with absorbance at the excitation wavelength being in the range of 0.10–0.12. The solvents (toluene, acetonitrile, DMSO, hexane) were purified and dried according to common procedures [27].

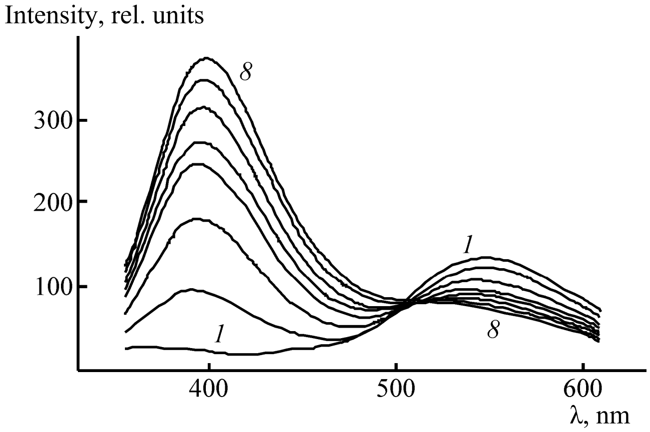


Fig. 5. Fluorescence spectra of triazole **II** (toluene, c = 2×10^{-5} mol/L, λ_{ex} = 320 nm). (*1*) initial solution, (*2–8*) after sequential addition of DMSO, 0.05 mL at each step.

The quantum-chemical computations were performed via DFT with triparametric B3LYP potential in the split-valence basis 6-31G(d,p) [28] using GAUSSIAN-03 software package. The stationary points were identified by Hessian calculations. Graphical representations of structures used in this publication were prepared in GaussView 3 software [29]. Charges at atoms were calculated following the Mulliken population analysis.

4-Oxo-1,3-benzoxalinium perchlorate **I** and benzthiazoltriazol **II** were prepared according to [24] and [11], respectively.

2-[5-(2-Metoxyphenyl)-3-methyl-1,2,4-triazol-1-yl]-1,3-benzthiazol (IIIa). 2.3 g of Ag_2O was added to a solution of 0.31 g (1 mmol) of **II** in 20 mL of chloroform, and the mixture was refluxed during 15 min. Then, 0.16 mL of methyl iodide was added, and the mixture was further refluxed during 3 h. The mixture was then cooled down, the inorganic precipitate was filtered off, the mother liquor was stripped to dryness under vacuum, and the obtained residue was twice recrystallized from propanol-2. Yield 0.27 g (58%), colorless crystals, mp 152–154°C. IR spectrum, ν, cm^{-1}: 1436, 1466, 1503, 1519 (C=C), 1567, 1593, 1623 C=N). ^{1}H NMR spectrum, δ, ppm: 2.48 s (3H, CH_3), 2.67 s (3H, CH_3), 7.19–7.45 m (6H, H_{arom}), 7.59 t (1H, H_{arom}, ^{3}J 7.5 Hz), 8.16 d (1H, H_{arom}, ^{3}J 7.8 Hz). ^{13}C NMR spectrum, δ_{C}, ppm: 14.81 (CH_3), 16.13 (CH_3), 111.50 (C_{arom}), 116.86 (C_{arom}), 122.13 (C_{arom}), 125.00 (C_{arom}), 125.34 (C_{arom}), 125.86 (C_{arom}), 125.93 (C_{arom}), 127.02 (C_{arom}), 132.00 (C_{arom}), 133.69 (C_{arom}), 135.86 ($C^{2''}_{\mathrm{thiaz}}$), 141.98 (C_{arom}), 150.67 (C^{5}_{triaz}), 151.30 (C_{arom}), 165.46 (C^{3}_{triaz}). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 136 (55), 190 (15), 275 (50), 281 (10) $[M - CH_3CN]^+$, 289 (13) $[M - HS]^+$, 322 (100) $[M]^+$. Found, %: C 44.30; H 3.30; N 42.40; S 6.70. $C_{17}H_{14}N_4OS$. Calculated, %: C 44.16; H 3.03; N 42.43; S 6.92. M 322.

{2-[2-(1,3-Benzthiazol-2-yl)-5-methyl-1,2,4-triazol-3-yl]phenyl}acetate (IIIb). 3 droplets of 70% $HClO_4$ were added to a stirred suspension of 0.31 g (1 mmol) of **II** in 2 mL of Ac_2O. The mixture warmed up, and the parent compound was dissolved. The mixture was incubated during 2 days at room temperature, and then diluted with 50 mL of water. After 1 day, the formed precipitate was filtered off, washed with water, and dried. The product was twice recrystallized from cyclohexane and once from heptane. Yield 0.19 g (54%), colorless crystals, mp 59–61°C. IR spectrum, ν, cm^{-1}: 1438, 1464, 1533 (C=C), 1550, 1597, 1614 (C=N), 1742, 1764 (C=O). ^1H NMR spectrum, δ, ppm: 1.85 s (3H, CH_3), 2.53 s (3H, CH_3), 7.30–7.82 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.36 (CH_3), 21.20 (CH_3), 121.51 (C_{arom}), 121.70 (C_{arom}), 123.06 (C_{arom}), 124.03 м (C_{arom}), 125.89 (C_{arom}), 126.02 (C_{arom}), 127.10 (C_{arom}), 131.85 m (C_{arom}), 132.12 м (C_{arom}), 133.91 (C_{arom}), 149.49 (C_{arom}), 150.95 (C_{arom}), 152.50 (C^5_{triaz}), 156.90 ($C^{2''}{}_{thiaz}$), 162.57 (C^3_{triaz}), 168.32 (C=O). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 148 (70), 189 (30), 291 (100) $[M - CH_3COO]^+$, 308 (64) $[MH - CH_3CO]^+$, 309 (15) $[M - CH_3CN]^+$, 350 (7) $[M]^+$. Found, %: C 62.40; H 4.50; N 15.40; S 9.40. $C_{18}H_{14}N_4O_2S$. Calculated, %: C 61.72; H 3.99; N 15.98; S 9.15. *M* 350.

{2-[2-(1,3-Benzthiazol-2-yl)-5-methyl-1,2,4-triazol-3-yl]phenyl}4-mehtylbenzolsulfonate (IIIc). 2.76 g (4 mmol) of the freshly calcined potassium carbonate and 0.19 g (1 mmol) of tosyl chloride were sequentially added to a solution of 0.31 g (1 mmol) of **II** in 10 mL of butanone, and the mixture was refluxed during 3 h. After cooling down to room temperature, 20 mL of icy water was added, the formed precipitate was filtered off and twice recrystallized from propanol-2. Yield 0.23 g (51%), colorless crystals, mp 158–160°C. IR spectrum, ν, cm^{-1}: 1168, 1368 (SO_2), 1440, 1457, 1507 (C=C), 1541, 1599, 1616 (C=N). ^1H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 2.38 s (3H, CH_3), 7.07 d (2H, H_{arom}, *J* 7.6 Hz), 7.30–7.65 m (9H, H_{arom}), 7.82 d (1H, H_{arom}, *J* 5.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.24 (CH_3), 22.08 (CH_3), 121.87 (C_{arom}), 122.88 (C_{arom}), 123.78 (C_{arom}), 124.16 (C_{arom}), 125.97 (C_{arom}), 126.95 (C_{arom}), 127.47 (C_{arom}), 128.31 (C_{arom}), 130.11 (C_{arom}), 131.95 (C_{arom}), 132.29 (C_{arom}), 132.50 (C_{arom}), 134.13 (C_{arom}), 145.58 (C_{arom}), 147.68 (C_{arom}), 150.85 (C_{arom}), 151.20 (C^5_{triaz}), 156.81 ($C^{2''}{}_{thiaz}$), 162.13 (C^3_{triaz}). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 148 (81), 189 (27), 238 (15), 291 (100) $[M - TsO]^+$, 308 (64) $[MH - Ts]^+$, 462 (5) $[M]^+$. Found, %: C 59.60; H 3.90; N 12.10; S 13.80. $C_{23}H_{18}N_4O_3S$. Caclulated, %: C 59.74; H 3.89; N 12.12; S 13.87. *M* 462.

Bis{2-[1-(1,3-benzthiazol-2-yl)-3-methyl-1*H*-1,2,4-triazol-5-yl]phenolato}beryllium (IVa). Solution of 0.14 g (0.5 mmol) of beryllium sulfate tetrahydrate was added to a hot solution of 0.3 g (1 mmol) of **II** and 0.04 g (1 mmol) sodium hydroxide in 10 mL of methanol. The formed precipitate was boiled during 3 h, filtered off, and twice washed with 10 mL of boiling methanol. The complex was recrystallized from the methylene chloride–methanol (2 : 1) and then from the toluene – heptane (1 : 1). Yield 52%, yellow crystals, mp > 260°C. IR spectrum, ν, cm^{-1}: 1420, 1438, 1473, 1490 (C=C), 1547, 1575, 1610 (C=N). ^1H NMR spectrum, δ, ppm: 2.09 s (3H, CH_3), 6.52 t (1H, H_{arom}, *J* 7.5 Hz), 7.03 d (1H, H_{arom}, *J* 7.5 Hz), 7.32–7.65 m (4H, H_{arom}), 7.96 d (1H, H_{arom}, *J* 7.5 Hz); 8.13 d (1H, H_{arom}, *J* 7.5 Hz). Mass spectrum (ESI), *m*/*z* (I_{rel}, %): 314 (23) $[M - L]^+$, 622 (100) $[M + H]^+$, 644 (35) $[M + Na]^+$. Found, %: C 61.20; H 4.00; N 10.60; Be 1.80. $C_{32}H_{22}N_8O_2S_2Be$. Calculated, %: C 61.64; H 3.53; N 10.28; Be 1.44. *M* 621.

Bis{2-[1-(1,3-benzthiazol-2-yl)-3-methyl-1*H*-1,2,4-triazol-5-yl]phenolato}copper(II) (IVb). 0.1 g (0.5 mmol) of copper(II) acetate monohydrate in 6 mL of methanol was added to a hot solution of 0.3 g (1 mmol) of **II** in 5 mL of methanol. The formed precipitate was boiled during 3 h, filtered off, and washed twice with 10 mL of boiling methanol. The complex was recrystallized from DMSO. Yield 0.24 g (37%), brown crystals, mp >260°C. IR spectrum, ν, cm^{-1}: 1439, 1470, 1507, 1533 (C=C), 1549, 1563, 1610 (C=N). Mass spectrum (ESI), *m*/*z* (I_{rel}, %): 338 (34) $[M - L]^+$, 646 (100) $[M + H]^+$, 668 (27) $[M + Na]^+$. Found, %: C 56.40; H 2.90; Cu 10.20; N 17.50; S 10.40. $C_{30}H_{22}CuN_8O_2S_2$. Calculated, %: C 55.81; H 3.40; Cu 9.84; N 17.34; S 9.91. *M* 645.

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