# Synthesis, structure, and photoluminescence of 5-phenyl-2-pyridyl-5,6-dihydro[1,2,4]triazolo[1,5-*c*]quinazolines

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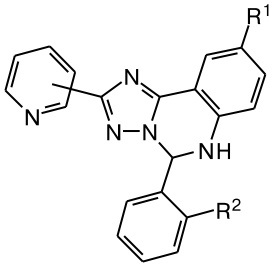
The reactions of salicylaldehyde and benzoic aldehyde with 5-(2-aminophenyl)-3-pyridyl-1*H*-1,2,4-triazoles were studied. The reaction products are 5-phenyl-2-pyridyl-5,6-dihydro[1,2,4]triazolo[1,5-*c*]quinazolines. The structures of the synthesized compounds were determined by IR spectroscopy and $^1$H and $^{13}$C NMR spectroscopy. The luminescence properties of solutions and solid samples were studied.

**Key words:** 5-(2-aminophenyl)-1*H*-1,2,4-triazoles, 5,6-dihydro[1,2,4]triazolo[1,5-*c*]-quinazolines, luminescence.

The study of the relationship between the specific features of the structure of a substance and its spectral properties is an urgent problem of molecular photonics and physical organic chemistry.[1] Correlations structure—property were revealed for many organic luminophores. Nevertheless, active studies in this area are being continued at present, which is due to their wide use in materials science, analytical chemistry, and medicinal chemistry.[2—4]

We have recently[5] described the coordination compound of zinc with the condensation product of salicylaldehyde and 5-(2-aminophenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole, exhibiting intense photo- and electroluminescence. However, no structural and spectral characteristics of the free ligands were studied. In the present work, we studied the structure and fluorescence properties of solutions and solid samples of the condensation products of salicylaldehyde and benzoic aldehyde with 5-(2-amino-4-R-phenyl)-3-pyridyl-1*H*-1,2,4-triazoles (**1**—**8**).




**1—8**

| Compound | Position Py | $R^1$ | $R^2$ | Compound | Position Py | $R^1$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| **1** | 2 | H | OH | **5** | 2 | F | OH |
| **2** | 3 | H | OH | **6** | 2 | Cl | OH |
| **3** | 4 | H | OH | **7** | 2 | Br | OH |
| **4** | 2 | Me | OH | **8** | 2 | H | H |

## Results and Discussion

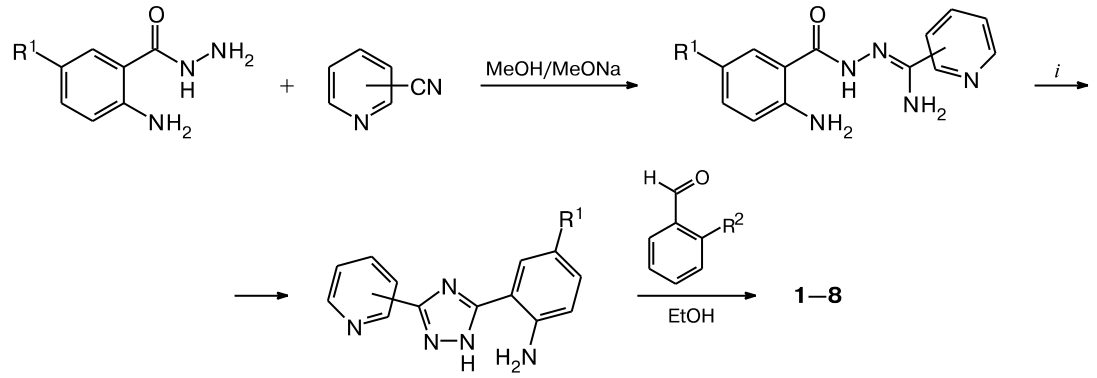
The starting 5-(2-amino-4-R-phenyl)-3-pyridyl-1*H*-1,2,4-triazoles were synthesized by the reaction of nitriles of pyridinecarboxylic acids with hydrazides with the corresponding 2-aminobenzoic acids.[6] The studied compounds were prepared by the reaction of aromatic aldehydes with 5-(2-aminophenyl)-3-pyridyl-1*H*-1,2,4-triazoles in an alcoholic solution (Scheme 1).

It was established that the reaction is general and affords 5-phenyl-2-pyridyl-5,6-dihydro[1,2,4]triazolo-[1,5-*c*]quinazolines **1**—**8**. It has earlier[7,8] been found by X-ray diffraction analysis that in coordination compounds the condensation product of salicylaldehyde with 5-(2-aminophenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole can exist in two isomeric forms: linear azomethine form (**A**) and cyclic dihydrotriazaindolizine form (**B**).

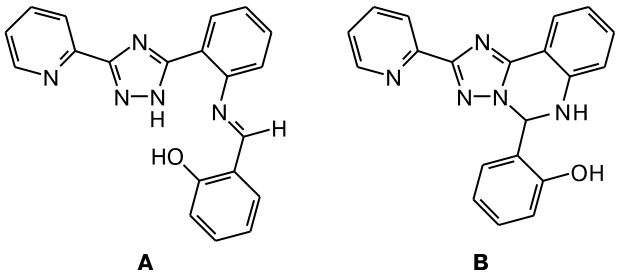
The data of NMR and IR spectroscopy indicate that in the free state compounds **1**—**8** exist in cyclic form **B**. The IR spectra of the synthesized substances in the region of 3270—3400 cm$^{-1}$ exhibit bands attributed to the N—H group stretching vibrations. The bands are insignificantly broadened due to hydrogen bond formation. The skeletal stretching vibrations of the benzene, pyridyl, and triazole rings are detected at 1512—1602 cm$^{-1}$. The $^1$H NMR spectra of compounds **1**—**8** are characterized by the signal of the proton of the C(5)H group at δ 7.10—7.25. The

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 93—96, January, 2012.

**Scheme 1**




*i*. Ethane-1,2-diol.



**A** **B**

singlet signal from the hydrogen atom of the azomethine group at δ 8.7—9.3 is absent, which is a ponderable argument for the formation of the cyclic form.[9] The $^1$H NMR spectra contain no signal of the hydrogen atom of the triazole cycle, which usually appears at δ 13—14, and the signal of the hydrogen atom of secondary amine is detected at δ 6.99—6.78. The cyclic form is also favored by the $^{13}$C NMR spectra in which the signals of the C(5)H carbon atom are observed at δ 67, whereas the signals of the carbon atom of the HC=N group usually appear at δ 157—164.[10]

The absorption and luminescence spectra of solid samples and solutions of the synthesized compounds were studied at ambient temperature. The maximum light absorption for compounds **1**—**3** is detected at 319—354 nm (Table 1), indicating the possibility of luminescence excitation by the absorption of the intense mercury line with a maximum at 365 nm. The studied compounds in the solid state weakly fluoresce in the visible region with emission maximum at 430—450 nm. The exceptions are compound **3**, whose spectrum contains the emission maximum at 540 nm, and compound **1**, which nearly does not luminesce in the solid state (Table 2). The variation of the substituents in the aromatic rings of compounds **4**—**8** results in an insignificant long-wavelength shift of the luminescence maximum. The maximum bathochromic shift is observed for the fluorinated derivative (compound **5**). The low luminescence intensity of the solid samples (except for compound **2**) can be due to considerable nonradiative energy losses because of intermolecular interactions.

Solutions of compounds **1** and **4**—**8** in DMSO are characterized by one-band luminescence and Stokes shifts usual for organic compounds. The luminescence maximum is poorly sensitive to the nature of the substituent in aromatic rings (see Table 2).

The luminescence spectra of compound **3** were studied in solvents of various polarity. It was found that one max-

**Table 1.** Parameters of the absorption and excitation spectra of compounds **1**—**3**

| Compound | Absorption | | Excitation | |
|---|---|---|---|---|
| | $\lambda_{max}$/nm | $A$ | $\lambda_{max}$/nm | $I$/quantum s$^{-1}$ |
| **1** | 348 | 0.242 | 390 | 682568 |
| **2** | 319 | 0.149 | 365 | 1560000 |
| **3** | 354 | 0.348 | 406 | 67500 |

**Table 2.** Parameters of the luminescence spectra of compounds **1**—**8** (the $I_{lum}$ values are reduced to the same experimental conditions separately for solid samples and solutions)

| Compound | Solid sample | | Solution in DMSO ($C = 1 \cdot 10^{-3}$ mol L$^{-1}$) | | |
|---|---|---|---|---|---|
| | $\lambda_{max}$/nm | $I_{lum}$ | $\lambda_{max}$/nm | $I_{lum}$ | φ* (%) |
| **1** | 440 | 1 | 430 | 105 | 17 |
| **2** | 430 | 110 | 420 | 120 | 36 |
| **3** | 540 | 8 | 528 | 100 | 5 |
| **4** | 440 | 6 | 452 | 131 | 11 |
| **5** | 450 | 17 | 453 | 191 | 15 |
| **6** | 430 | 20 | 448 | 115 | 12 |
| **7** | 430 | 6 | 448 | 53 | 12 |
| **8** | 450 | 20 | 430 | 110 | 21 |

* Luminescence quantum yield.

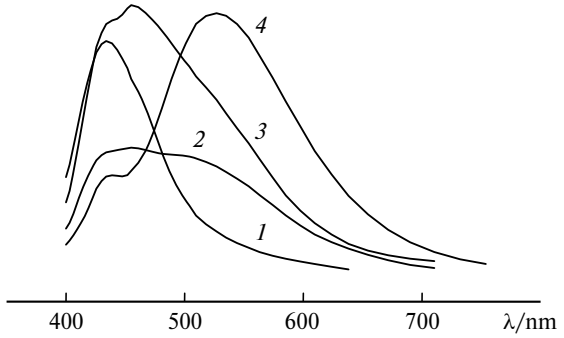



**Fig. 1.** Luminescence spectra of solutions of compound **3** in various solvents: THF (*1*), MeCN (*2*), DMF (*3*), and DMSO (*4*).

imum is observed in the luminescence spectrum in low-polarity THF (Fig. 1, curve *1*). On going to solvents of higher polarity (DMSO, DMF, acetonitrile) (Fig. 1, curves *2*—*4*), two emission maxima appear, which can be due to the existence of two tautomers in the excited state.

Thus, it was found that 5-phenyl-2-pyridyl-5,6-dihydro[1,2,4]triazolo[1,5-*c*]quinazolines represent a new class of compounds luminescing in the solid state and in solutions. These compounds can be recommended for use as complexation substances in luminescence analysis and as molecular probes and fluorescent labels in biological assays.

## Experimental

Nitriles of pyridinecarboxylic acids (Merck) were used as the starting compounds. Hydrazides of 2-aminocarboxylic acids were synthesized according to earlier described procedures.[11] Solvents were purified by standard procedures.[12]

IR spectra were recorded in the 4000—400 $cm^{-1}$ region on a Nicollet Nexus 470 spectrophotometer (KBr pellets). $^1H$ and $^{13}C$ NMR spectra were obtained on a Bruker VXR-400 spectrometer ($^1H$, 400 MHz; $^{13}C$, 75 MHz) using DMSO-$d_6$ as a solvent and $Me_4Si$ as an internal standard. Absorption spectra were studied on a Lambda-9 UV/VIS/NIR spectrophotometer (Perkin—Elmer). The luminescence spectra of solid samples were detected on an SDL-1 diffraction spectrometer (LOMO, Russia) with a FEU-79 photomultiplier tube. Excitation spectra were recorded on a Fluorolog-FL 3-22 instrument with a xenon lamp (450 W). The standard for measuring quantum yields was quinine sulfate in a 0.1 *M* solution of $H_2SO_4$.

**Synthesis of 5-phenyl-2-pyridyl-5,6-dihydro[1,2,4]triazolo-[1,5-*c*]quinazolines 1—8 (general procedure).** 5-(2-Amino-4-R-phenyl)-3-pyridyl-1*H*-1,2,4-triazole (4 mmol) was dissolved in hot ethanol (20 mL), and aldehyde (4.2 mmol) was added. The reaction mixture was magnetically stirred for 1 h on heating. The solution was cooled down, and the precipitate that formed was filtered off, washed with cold ethanol, and dried *in vacuo*. The yields of the products were 1.0—1.2 g (75—87% based on the starting triazole).

**2-(2-Pyridin-2-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (1).** M.p. 237 °C (EtOH). The yield was 85%. Found (%): C, 70.22; H, 4.28. $C_{20}H_{15}N_5O$. Calculated (%): C, 70.38; H, 4.40. $^1H$ NMR, δ: 10.1 (s, 1 H, OH); 8.65 (d, 1 H arom., $J$ = 4.4 Hz); 8.12 (d, 1 H arom., $J$ = 8.0 Hz); 7.90 (dt, 1 H arom., $J$ = 7.2 Hz, $J$ = 0.8 Hz); 7.80 (d, 1 H arom., $J$ = 7.2 Hz); 7.40 (m, 2 H arom.); 7.27 (t, 1 H arom., $J$ = 8.4 Hz); 7.24—7.19 (m, H arom. + + C(5)H); 6.95 (m, 2 H arom. + 1 H, NH); 6.85 (t, 1 H arom., $J$ = 7.6 Hz); 6.80 (t, 1 H arom., $J$ = 7.2 Hz). $^{13}C$ NMR, δ: 161.6, 155.2, 151.1, 150.0, 149.9, 143.7, 137.5, 132.3, 130.6, 127.7, 126.1, 124.6, 124.4, 122.2, 119.5, 118.3, 116.3, 115.0, 110.0, 67.7. IR, ν/$cm^{-1}$: 3270, 1629, 1597, 1523, 1457, 1361, 1292, 1281, 1236, 1159, 742.

**2-(2-Pyridin-3-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (2).** M.p. 245 °C (EtOH). The yield was 81%. Found (%): C, 70.29; H, 4.11. $C_{20}H_{15}N_5O$. Calculated (%): C, 70.38; H, 4.40. $^1H$ NMR, δ: 10.04 (s, 1 H, OH); 9.15 (s, 1 H arom.); 8.61 (d, 1 H arom., $J$ = 4.8 Hz); 8.30 (dt, 1 H arom., $J$ = 8.0 Hz, $J$ = 0.8 Hz); 7.78 (d, 1 H arom., $J$ = 8.0 Hz); 7.48 (dd, 1 H arom., $J$ = 7.4 Hz, $J$ = 8.2 Hz); 7.37 (s, 1 H, C(5)H); 7.24 (dt, 1 H arom., $J$ = 8.2 Hz, $J$ = 0.8 Hz); 7.18—7.05 (m, 2 H arom.); 6.88 (t, 2 H arom., $J$ = 7.6 Hz); 6.82—6.78 (m, 1 H arom. + NH); 6.71 (t, 1 H arom., $J$ = 7.6 Hz). $^{13}C$ NMR, δ: 159.7, 155.3, 151.7, 150.9, 149.9, 143.7, 138.3, 132.6, 130.7, 127.5, 126.0, 124.4, 123.9, 120.6, 119.5, 118.3, 116.2, 115.1, 109,8, 67.9. IR, ν/$cm^{-1}$: 3402, 1624, 1602, 1512, 1458, 1412, 1350, 1248, 750.

**2-(2-Pyridin-4-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (3).** M.p. 251 °C (EtOH). The yield was 87%. Found (%): C, 70.03; H, 4.54. $C_{20}H_{15}N_5O$. Calculated (%): C, 70.38; H, 4.40. $^1H$ NMR, δ: 10.04 (br.s, 1 H, OH); 8.66 (d, 2 H arom., $J$ = 5.6 Hz); 7.90 (d, 2 H arom., $J$ = 6.0 Hz); 7.79 (d, 1 H arom., $J$ = 6.8 Hz); 7.40 (s, 1 H arom.); 7.25 (t, 1 H, $J$ = 7.6 Hz); 7.20—7.16 (m, 1 H arom.+ +1 H (C(5)H)); 6.95—6.85 (m, 3 H arom. + NH); 6.73 (t, 1 H arom., $J$ = 7.2 Hz). $^{13}C$ NMR, δ: 159.6, 155.4, 151.3, 150.8, 150.0, 147.5, 143.7, 134.1, 132.5, 130.6, 127.5, 126.2, 124.5, 124.4, 119.7, 118.4, 116.3, 115.0, 109.7, 67.6. IR, ν/$cm^{-1}$: 3402, 1624, 1600, 1512, 1458, 1414, 1350, 1248, 750.

**2-(9-Methyl-2-pyridin-2-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (4).** M.p. 209 °C (EtOH). The yield was 75%. Found (%): C, 71.09; H, 4.66. $C_{21}H_{17}N_5O$. Calculated (%): C, 70.98; H, 4.79. $^1H$ NMR, δ: 10.03 (s, 1 H, OH); 8.61 (d, 1 H arom., $J$ = 5.2 Hz); 8.08 (d, 1 H arom., $J$ = 10.8 Hz); 7.90 (dt, 1 H arom., $J$ = 6.8 Hz, $J$ = 0.8 Hz); 7.64 (s, 1 H arom.); 7.43 (dt, 1 H arom., $J$ =5.6 Hz, $J$ = 0.8 Hz); 7.25—7.15 (m, 1 H arom. + + 1 H, C(5)H); 7.12—6.95 (m, 1 H arom. + NH); 6.91—6.81 (m, 3 H arom.); 6.73 (t, 1 H arom., $J$ = 7.6 Hz); 2.27 (s, 3 H, $CH_3$). IR, ν/$cm^{-1}$: 3386, 1630, 1600, 1516, 1504. 1418, 1350, 1290, 1248, 750.

**2-(9-Fluoro-2-pyridin-2-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (5).** M.p. 241 °C (EtOH). The yield was 80%. Found (%): C, 67.02; H, 3.79. $C_{20}H_{14}FN_5O$. Calculated (%): C, 66.85; H, 3.90. $^1H$ NMR, δ: 10.05 (br.s, 1 H, OH); 8.61 (d, 1 H arom., $J$ = 4.0 Hz); 8.07 (d, 1 H arom., $J$ = 7.2 Hz); 7.89 (dt, 1 H arom., $J$ = 7.2 Hz, $J$ = 1.6 Hz); 7.54 (dd, 1 H arom., $J$ = 8.4 Hz, $J$ = 2.8 Hz); 7.42 (m, 1 H arom.); 7.34 (s, 1 H arom.); 7.20—7.05 (m, 2 H arom. + 1 H, C(5)H); 6.95—6.82 (m, 2 H arom. + NH); 6.75 (t, 1 H arom., $J$ = 7.6 Hz). IR, ν/$cm^{-1}$: 3280, 1638, 1600, 1522, 1456, 1422, 1356, 1284, 1196, 746.

**2-(9-Chloro-2-pyridin-2-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (6).** M.p. 235 °C (EtOH). The yield was 84%.

Found (%): C, 63.72; H, 3.68. $C_{20}H_{14}ClN_5O$. Calculated (%): C, 63.91; H, 3.73. $^1$H NMR, δ: 10.02 (br.s, 1 H, OH); 8.60 (d, 1 H arom., $J$ = 6.0 Hz); 8.08 (d, 1 H arom., $J$ = 8.0 Hz); 7.89 (dt, 1 H arom., $J$ = 7.6 Hz, $J$ = 1.2 Hz); 7.72 (d, 1 H arom., $J$ =2.4 Hz); 7.59 (s, 1 H arom.); 7.42 (m, 1 H arom.); 7.28 (m, 1 H arom.); 7.25—7.15 (m, 1 H arom. + 1 H, C(5)H); 6.96 (d, 1 H, NH, $J$ = 7.2 Hz); 6.87 (d, 2 H arom., $J$ = 7.6 Hz); 6.75 (t, 1 H arom., $J$ = 7.2 Hz). IR, ν/cm$^{-1}$: 3266, 1626, 1600, 1522, 1458, 1354, 1282, 1152, 752.

**2-(9-Bromo-2-pyridin-2-yl-5,6-dihydro[1,5-*c*]quinazolin-5-yl)phenol (7).** M.p. 237 °C (EtOH). The yield was 87%. Found (%): C, 57.25; H, 3.24. $C_{20}H_{14}BrN_5O$. Calculated (%): C, 57.14; H, 3.33. $^1$H NMR, δ: 10.05 (br.s, 1 H, OH); 8.60 (d, 1 H arom., $J$ = 4.4 Hz); 8.07 (d, 1 H arom., $J$ = 7.6 Hz); 7.90—7.82 (m, 2 H arom.); 7.61 (s, 1 H arom.); 7.40—7.30 (m, 2 H arom.); 7.20—7.10 (m, 1 H arom. + 1 H, C(5)H); 6.97 (d, 1 H, NH, $J$ = 7.6 Hz); 6.87 (d, 1 H arom., $J$ = 8.4 Hz); 6.82 (d, 1 H arom., $J$ = 8.0 Hz); 6.75 (t, 1 H arom., $J$ = 7.2 Hz). IR, ν/cm$^{-1}$: 3268, 1626, 1600, 1520, 1458, 1354, 1284, 1234, 1152, 752.

**5-Phenyl-2-pyridin-2-yl-5,6-dihydro[1,2,4]triazolo[1,5-*c*]-quinazoline (8).** M.p. 216 °C (EtOH). The yield was 76%. Found (%): C, 73.67; H, 4.65. $C_{20}H_{15}N_5$. Calculated (%): C, 73.85; H, 4.62. $^1$H NMR, δ: 8.62 (d, 1 H arom., $J$ =4.4 Hz); 8.07 (d, 1 H arom., $J$ = 8.0 Hz); 7.89 (dt, 1 H arom., $J$ = 7.6 Hz, $J$ = 1.6 Hz); 7.79 (d, 1 H arom., $J$ = 7.6 Hz); 7.69 (s, 1 H arom.); 7.44—7.36 (m, 5 H arom. + 1 H, C(5)H); 7.29 (dt, 1 H arom., $J$ = 8.4 Hz, $J$ = 1.6 Hz); 6.99 (d, 1 H, NH, $J$ = 1.2 Hz); 6.92 (d, 1 H arom., $J$ = 8.0 Hz); 6.86 (t, 1 H arom., $J$ = 7.6 Hz). $^{13}$C NMR, δ: 160.9, 154.7, 150.2, 150.0, 149.2, 142.9, 138.3, 132.3, 130.8, 126.2, 126.1, 124.4, 124.4, 122.2, 119.3, 118.5, 116.3, 114.9, 109.9, 67.6. IR, ν/cm$^{-1}$: 3296, 1624, 1590, 1528, 1480, 1412, 1356, 1152, 740.

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*Received February 21, 2011;*
*in revised form August 10, 2011*