## Synthesis, photochemical and luminescent properties of (E)-2-(2-hydroxyarylethylene)-3-phenylquinazolin-4(3H)-ones\*

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Photoinduced transformations of 2-styrylquinazolinones in solutions were studied using absorption and NMR spectroscopy methods. A possibility of control of the photochemical isomerization rate of quinazolinone 2-(hydroxyaryl)ethenyl derivatives by changing the pH of the medium was demonstrated. The bases and the solvent nature also affect the luminescence intensity of solutions of these compounds in the wavelength range of 550-650 nm. The differences in the steric organization of the *ortho*-hydroxystyryldiazinone system in crystals and in solutions related to the turn of the aryl group were found. Their influence on the competing processes of luminescence and photochemical transformation of the ethylene fragment were shown. The fact of reversible photo/thermal E-Z-isomerization was established for (E)-2-(2-hydroxystyryl)-3-phenylquinazolin-4(3H)-one.

Key words: (E)-2-styrylquinazolin-4(3*H*)-ones, *ortho*-hydroxystyrylquinazolinones, luminescence, reversible photo/thermal isomerization, photoswitching.

Diarylethenes and their heterocyclic analogues form the basis of modern electroluminescent and photochromic materials, successfully used in nonlinear optics, lasers with tunable frequency, optoelectronic devices for recording and storage of information, molecular photoswitches.<sup>1,2</sup> Among hetarylstilbenes, their unsymmetric derivatives $^{3,4}$  are of particular interest. Owing to the contribution of the  $n,\pi^*$ -state, the presence of an acceptor azine (azinone) core in addition to the donor (aryl) one in stilbene molecules can have a considerable influence on photochemical and photophysical behavior of the luminophores.<sup>5</sup> However, there are fewer publications on the studies of the corresponding systems than of the symmetric (het)arylethenes.<sup>4</sup> In particular, there are several works on the synthesis of (E)-2-styrylquinazolin-4(3H)-ones and the study of their photophysical properties.<sup>4,6–10</sup> It should be noted that compounds of this type with a specific emission ability and a tendency to a photoinduced E-Z-isomerization<sup>9,10</sup> can be quite promising for the development of pH-sensitive photochromic materials. We think that the introduction of a hydroxy group at the ortho-position

of the arylethenyl fragment of quinazolinones can generate photocontrolled processes related to the E-Z-isomerization with a proton transfer in the course of tautomeric transformations and heterocyclization to the corresponding spiropyrans.

## Experimental

IR spectra were recorded on a Perkin-Elmer Spectrum One IR Fourier-transform spectrometer using a diffuse reflectance sampling accessory (DRA). Electron absorption spectra were recorded on a UV-2401 PC double-beam spectrophotometer (Shimadzu, Japan) in the range of 190-700 nm with the wavelength setting accuracy of ±0.3 nm using a Shimadzu Scan standard program. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer with mutually perpendicular beams, the wavelength setting accuracy of 0.5 nm. The measurements were carried out in the range of 190-800 nm in SUPRASIL 111-QS 10 quartz cells (Hellma, Germany), the bandwidth around the stationary point of excitation/emission was 10 nm. The wavelength of the excitation stationary point was assigned based on the maximum in absorption and emission spectra each time, the wavelength of the emission stationary point, based on the maximum in excitation spectra. The PEM bias was 600 V. The solvent luminescence was taken into account in the spectra. The relative quantum yields of solutions were measured at 22±1 °C according to the procedure, given at

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2467–2477, November, 2014. 1066-5285/14/6311-2467 © 2014 Springer Science+Business Media, Inc.

<sup>\*</sup> Dedicated to Academician of the Russian Academy of Sciences Yu. N. Bubnov on the occasion of his 80th birthday and to the 60th anniversary of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

www.jyhoriba.co.uk (Jobin Yvon Ltd. 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ UK). The control samples were fluoresceine<sup>11</sup> ( $\Phi_{abs} = 0.85$ ) in 0.1 N aqueous solution of KOH and quinine bisulfate<sup>11</sup> ( $\Phi_{abs} = 0.55$ ) in 0.1 N aqueous solution of H<sub>2</sub>SO<sub>4</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker DRX-400 (400 and 100 MHz) and Bruker AVANCE-500 (500 and 126 MHz) spectrometers in DMSO-d<sub>6</sub>, using TMS and DMSO-d<sub>6</sub> ( $\delta_C$  39.5) as references. <sup>1</sup>H and <sup>13</sup>C signals in the NMR spectra were assigned using 2D experiments <sup>1</sup>H–<sup>1</sup>H COSY, <sup>1</sup>H–<sup>1</sup>H NOESY, <sup>1</sup>H–<sup>13</sup>C HSQC, and HMBC. Electron impact mass spectra of compounds were recorded on a Shimadzu GCMS-QP2010 Ultra EI instrument (70 eV). Melting points were measured on a Boetius heating microstage. Thinlayer chromatography was carried out on Silufol UV-254 plates. Spots were visualized under the light of a low-pressure mercury lamp (6 W) or in iodine vapors.

**2-Methyl-3-phenylquinazolin-4(3***H***)-one (1).** Aniline (0.7 g, 7.5 mmol) and  $P_2O_5$  (1 g) were added to 2-methyl-3,1-benz-oxazin-4-one (1.2 g, 7.5 mmol) (obtained by reflux of anthranilic acid in freshly distilled acetic anhydride<sup>12</sup>) in pyridine (15–20 mL). The reaction mixture was heated for 26 h at 90–95 °C. After the reaction reached completion, the solvent was evaporated, water (50 mL) was added to the residue. The product was filtered off and purified on a chromatographic column (SiO<sub>2</sub>), eluent ethyl acetate—hexane, 3 : 2. The yield was 1.5 g (89%). Analytical characteristics of this compound agreed with those given in the literature.<sup>13</sup>

(*E*)-2-Styrylquinazolin-4(3*H*)-ones (general method). A corresponding aldehyde 2a-d(1.7 mmol) and an equimolar amount of H<sub>3</sub>BO<sub>3</sub> (1.3 mmol) were added to compound 1 (0.3 g, 1.3 mmol) in acetic acid (30 mL). The reaction mixture was refluxed for 6–8 h. After the reaction reached completion, the solvent was evaporated, the product was purified by chromatography from different impurities, first of all, of the *Z*-isomer formed in small amounts (2–7%). Chromatographic separation was carried out on a column with SiO<sub>2</sub>, eluent ethyl acetate—hexane, the proportion of concentrations from 1 : 4 to 4 : 1, respectively. The target product was crystallized from ethanol (3a–c) or acetonitrile (3d). Analytical characteristics of (*E*)-3-phenyl-2-styryl-quinazolin-4(3*H*)-one (3a) (93% yield, 0.4 g) and (*E*)-2-(2-(naphthalen-1-yl)vinyl)-3-phenylquinazolin-4(3*H*)-one (3b) (89% yield, 0.43 g) agreed with those given in the works.<sup>10,13</sup>

(E)-2-(2-Hydroxystyryl)-3-phenylquinazolin-4(3H)-one (E-3c). The yield was 82% (0.36 g), m.p. 275-276 °C. <sup>1</sup>H NMR  $(500 \text{ MHz}, \text{DMSO-d}_6), \delta: 6.56 (d, 1 \text{ H}, \text{H}(\alpha), J = 15.6 \text{ Hz}); 6.76$ (t, 1 H, H(19), J = 7.5 Hz); 6.84 (br.d, 1 H, H(17), J = 7.9 Hz);7.12-7.17 (m, 2 H, H(18), H(20)); 7.45 (dm, 2 H, H(10), H(14), *J* = 7.1 Hz); 7.52 (ddd, 1 H, H(6), *J* = 7.8 Hz, *J* = 7.2 Hz, *J* = = 0.7 Hz); 7.55–7.64 (m, 3 H, H(11), H(13), H(12)); 7.78 (br.d, 1 H, H(8), J = 8.0 Hz); 7.87 (ddd, 1 H, H(7), J = 8.0 Hz, J = 7.2Hz, J = 1.1 Hz); 8.08 (d, 1 H, H( $\beta$ ), J = 15.6 Hz); 8.13 (dd, 1 H, H(5), J = 7.8 Hz, J = 1.1 Hz); 10.12 (s, 1 H, OH). <sup>13</sup>C NMR (125.76 MHz, DMSO-d<sub>6</sub>), δ: 116.11 (C(17)); 119.39 (C(19)); 119.86 (C(α)); 120.43 (C(4a)); 121.69 (C(15)); 126.25 (C(6)); 126.38 (C(5)); 127.10 (C(8)); 128.86 (C(20)); 128.92 (C(10), C(14)); 129.02 (C(12)); 129.58 (C(11), C(13)); 130.81 (C(18)); 134.67 (C(7)); 135.42 (C(β)); 137.24 (C(9)); 147.54 (C(8a)); 152.18 (C(2)); 156.60 (C(16)); 161.36 (C(4)). IR (DRA), v/cm<sup>-1</sup>: 599, 650; 693, 714, 746, 770 (Arom); 855, 910, 981, 1014, 1094, 1155, 1232, 1246, 1304, 1351, 1455, 1470, 1489; 1546, 1569, 1602, 1628 (C=C, C=N); 1655, 1667 (C=O); 3036, 3064

 $(C_{Arom}-H)$ ; 3320 (OH). Found (%): C, 77.58; H, 4.77; N, 8.21.  $C_{22}H_{16}N_2O_2$ . Calculated (%): C, 77.63; H, 4.74; N, 8.23.

A solution of *E*-3c in a 20-fold excess of the base  $(Me_4NOH \cdot 5H_2O)_{20}$ . <sup>1</sup>H NMR (500 MHz, DMCO-d<sub>6</sub>),  $\delta$ : 5.85 (ddd, 1 H, H(19), J = 7.5 Hz, J = 6.8 Hz, J = 1.0 Hz); 6.16 (dd, 1 Hz); 6.16 (dd,1 H, H(17), J = 8.4 Hz, J = 1.0 Hz); 6.40 (d, 1 H, H( $\alpha$ ), J = 16.3 Hz); 6.71 (ddd, 1 H, H(18), J = 8.4 Hz, J = 6.8 Hz, J = 1.8 Hz); 6.74-6.80 (m, 4 H, H(6), H(10), H(14), H(20)); 6.91 (tt, 1 H, H(12), J = 7.4 Hz, J = 1.1 Hz; 7.17 (ddd, 1 H, H(7), J = 8.4 Hz, J = 7.3 Hz, J = 1.7 Hz); 7.23 (m, 2 H, H(11), H(13)); 7.74  $(d, 1 H, H(\beta), J = 16.3 Hz); 7.97 (dd, 1 H, H(5), J = 7.3 Hz)$ J = 1.7 Hz); 8.73 (br.d, 1 H, H(8), J = 8.4 Hz). <sup>13</sup>C NMR (125.76 MHz, DMCO-d<sub>6</sub>), δ: 107.43 (C(19)); 111.60 (C(α)); 118.40 (C(8)); 118.59 (C(6)); 120.67 (C(12)); 121.66 (C(17)); 122.07 (C(10), C(14)); 123.26 (C(15)); 125.14 (C(4a)); 127.02 (C(20)); 128.42 (C(11), C(13)); 128.99 (C(7)); 129.95 (C(18));131.03 (C(5)); 136.13 (C( $\beta$ ));142.98 (C(8a)); 151.56 (C(9)); 153.68 (C(2)); 170.07 (C(4)); 172.02 (C(16)).

(Z)-2-(2-Hydroxystyryl)-3-phenylquinazolin-4(3H)-one (Z-3c). A solution of isomer E-3c (10 mg, 0.03 mmol) in DMSO-d<sub>6</sub> (1 mL) was placed into a 1-cm pathlength hermetically sealed quartz cell and exposed to the light of a DRSh-250 mercury discharge lamp (250 W) using an UFS-6 light filter at the distance of 13 cm with air cooling. The reaction progress was monitored by NMR. After 32 h of exposure, the <sup>1</sup>H NMR spectrum showed that the solution contained ~88% of photoinduced Z-isomer. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 5.92 (d, 1 H, H( $\alpha$ ), J = 12.4 Hz; 6.66 (d, 1 H, H( $\beta$ ), J = 12.4 Hz); 6.66 (t, 1 H, H(19), J = 7.3 Hz; 6.77 (d, 1 H, H(17), J = 7.9 Hz); 7.09 (ddd, 1 H, H(18), J = 7.9 Hz, J = 7.6 Hz, J = 1.7 Hz); 7.23 (dd, 1 H, H(20), J = 7.6 Hz, J = 0.9 Hz; 7.35 (dm, 2 H, H(10), H(14), J = 7.1 Hz); 7.49–7.53 (m, 4 H, H(11), H(13), H(12), H(8)); 7.55 (ddd, 1 H, H(6), J = 7.8 Hz, J = 7.2 Hz, J = 0.7 Hz); 7.81 (ddd, 1 H, H(7), J = 8.0 Hz, J = 7.2 Hz, J = 1.1 Hz); 8.15 (dd, 1 H, J = 1.1 Hz); 8.15 (dd, 1 Hz); 8.15 (dd, 1H(5), J = 7.8 Hz, J = 1.1 Hz; 9.80 (br.s, 1 H, OH).

(E)-2-[2-(2-Hydroxynaphthalen-1-yl)vinyl]-3-phenylquinazolin-4(3H)-one (3d). The yield was 72% (0.37 g), m.p. 257–258 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), δ: 6.91 (d, 1 H,  $H(\alpha)$ , J = 15.5 Hz; 7.14 (d, 1 H, H(17), J = 9.0 Hz); 7.33 (ddd, 1 H, H(20), J = 8.0 Hz, J = 7.1 Hz, J = 0.8 Hz); 7.46–7.51 (m, 3 H, H(10), H(14), H(21)); 7.53 (ddd, 1 H, H(6), J = 7.9 Hz, J = 6.8 Hz, J = 1.3 Hz); 7.56 (m, 1 H, H(12)); 7.62 (tm, 2 H, H(11), H(13), J = 7.5 Hz; 7.76 (d, 1 H, H(18), J = 9.0 Hz); 7.80 (dd, 1 H, H(19), J = 8.0 Hz, J = 1.0 Hz); 7.85 (dd, 1 H, H(8), J = 8.2 Hz, J = 1.3 Hz); 7.89 (ddd, 1 H, H(7), J = 8.2 Hz, J = 6.8 Hz, J = 1.5 Hz; 8.02 (br.d, 1 H, H(22), J = 8.6 Hz); 8.15  $(dd, 1 H, H(5), J = 7.9 Hz, J = 1.5 Hz); 8.62 (d, 1 H, H(\beta)),$ J = 15.5 Hz); 10.50 (s, 1 H, OH). <sup>13</sup>C NMR (125.76 MHz, DMSO-d<sub>6</sub>), δ: 113.24 (C(15)); 118.19 (C(17)); 120.41 (C(4a)); 121.95 (C(22)); 123.01 (C(20)); 123.44 (C( $\alpha$ )); 126.17 (C(6)); 126.39 (C(5)); 127.19 (C(21)); 127.24 (C(8)); 128.04 (C(18a)); 128.73 (C(19)); 128.95 (C(10), C(12)); 129.58 (C(11)); 131.13 (C(18)); 132.05 (C(β)); 132.51 (C(22a)); 134.66 (C(7)); 137.42 (C(9)); 147.63 (C(8a)); 152.72 (C(2)); 155.72 (C(16)); 161.46 (C(4)). IR (DRA), v/cm<sup>-1</sup>: 615, 624, 647; 689, 732, 754, 762, 795, 812 (Arom); 846, 859, 909, 973, 1014, 1032, 1079, 1117, 1180, 1208, 1219, 1248, 1270, 1329, 1344, 1430, 1469, 1491; 1511, 1534, 1608, 1625 (C=C, C=N); 1655 (C=O); 3062, 3075 (C<sub>Arom</sub>-H); 3343 (OH). Found (%): C, 79.64; H, 4.45; N, 7.17. C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>. Calculated (%): C, 79.98; H, 4.65; N, 7.17.

Studies of photophysical and photochemical properties of *E*-isomers 3a-d. Solvents were distilled and dried according to the standard procedures. Preparation and spectrophotometric studies of solutions were carried out in red light. Photochemical transformations in solutions were carried out in 1-cm pathlength hermetically sealed quartz cells in a photochemical reactor using a DRSh-250 mercury discharge lamp (250 W) with air cooling ( $23\pm2$  °C). Solutions were irradiated from a distance of 13 cm with a light flux, passing through the system of focusing lenses and SZS-7 or SZS-26 light filters (thermal filter) and UFS-6, in the short wavelength range of 364–456 nm. The lumen output (150 mW) was determined using an IMO-2N meter of average power and laser irradiation energy.<sup>14</sup> The light flux was directed into the meter using quartz optical fibers.

Kinetic studies by absorption spectroscopy. 1. Photochemical transformations of compounds  $E-3\mathbf{a}-\mathbf{d}$  ( $2\cdot 10^{-5}$  M) in *n*-butanol, acetonitrile, and dimethylformamide were carried out by recording UV spectra of irradiated solutions with allowance for the initial absorption every 2 s (in the case of isomers 3b,c), 1 min (3d), and 5 min (3a) until persistent state of the solutions.

2. Thermal transformations of photosteady solutions of compound Z-3c ( $2 \cdot 10^{-5} M$ ) thermostated at 35, 55, 65, and 75 °C were carried out by recording UV spectra every 10 min.

3. Spectrophotometric titration of solutions of E-3c,d (2 · 10<sup>-5</sup> *M*) with strong bases (Me<sub>4</sub>NOH or Bu<sup>t</sup>OK) were carried out until persistent state, using a series of solutions with the ratio of concentrations  $C_{E-3}$ :  $C_{\text{base}}$  from 1 : 1 to 1 : 25.

Kinetic studies by NMR. The studies by NMR were carried out for  $3 \cdot 10^{-5}$  M solutions of compounds E-3a-d in DMSO-d<sub>6</sub> (1 mL), using a technique similar to that described above for absorption spectroscopy. Photochemical transformations of compounds E-3a-d were carried out by recording <sup>1</sup>H NMR spectra of irradiated solutions every hour for 6 h and then every 4-6 h (over 30-32 h). In the case of compound E-3d, a mixture of photoproducts was separated by chromatography (eluent ethyl acetate-hexane, 1:2). The fractions with individual compounds 4a-c were characterized by mass spectrometry. MS (EI, 70 eV) **4a**, m/z ( $I_{rel}$  (%)): 390 [M]<sup>+</sup> (100), 373 [M - OH]<sup>+</sup> (71), 313  $[M - C_6H_5]^+$  (15), 298  $[M - C_6H_5NH]^+$  (37), 284 [M - $-C_6H_5-CHO]^+$  (5), 270 [M  $-C_6H_5NH-CO]^+$  (12), 244  $[M - C_6H_5NH - CO - CN]^+$  (45), 221  $[M - C_{12}H_8O - H]^+$  (26), 193  $[M - C_{12}H_8O - H - CO]^+$  (12), 168  $[M - C_{14}H_{10}N_2O]^+$ (36), 140  $[M - C_{14}H_{10}N_2O - CO]^+$  (29), 139  $[M - C_{14}H_{10}N_2O - CO]^+$  $CO-H]^+$  (55), 119 (40), 77 (80). MS (EI, 70 eV) 4b, m/z $(I_{rel}(\%))$ : 388 [M]<sup>+</sup> (100), 371 [M – OH]<sup>+</sup> (91), 359 [M – CHO]<sup>+</sup> (5), 269  $[M - C_6H_5NCO]^+$  (4), 221  $[M - C_{12}H_7O]^+$  (7), 194  $[M - C_{12}H_7O - HCN]^+$  (10), 179  $[M - C_{12}H_7O - NCO]^+$  (5), 139  $[M - C_{15}H_9N_2O_2]^+$  (15), 77 (38). MS (EI, 70 eV) 4c, m/z $(I_{rel} (\%))$ : 222 [M]<sup>+</sup> (100), 221 [M – H]<sup>+</sup> (91), 193 [M – CO]<sup>+</sup> (10), 167  $[M - CO - CN]^+$  (7), 129 (12), 119  $[M - C_7H_5N]^+$ (23), 102 (10), 77 (72).

X-ray diffraction studies. Crystals of compound *E*-3c were obtained by slow concentration of acetonitrile solution. X-ray diffraction analysis of the compound was carried out on a Xcalibur 3 automated diffractometer with a CCD detector (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, graphite monochromator,  $\omega/2\theta$  scan technique, with a 1° step) at 150(2) K. The set of reflections was obtained and processed using the CrysAlis software.<sup>15</sup> The structures were solved by direct method and refined by full-matrix least squares method first in isotropic and then in anisotropic approximation on  $F^2$  for all nonhydrogen atoms using the

 Table 1. Crystalographic data and parameters of the

 X-ray diffraction experiment for crystal *E*-3c

Parameter	Value
Molecular formula	$C_{22}H_{16}N_2O_2$
Molecular weight	340.37
Crystal system	Triclinic
Ζ	2
Space group	$P\overline{1}$
a/Å	8.8760(18)
b/Å	9.6168(14)
c/Å	10.734(2)
α/deg	91.142(15)
β/deg	113.02(2)
γ/deg	98.448(14)
$V/Å^3$	831.1(3)
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.360
F(000)	356
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.088
Crystal size/mm	0.25×0.20×0.15
Type/region of scanning	
on $\theta/\text{deg}$	3.03-26.42
Ranges of reflection	$-5 \le h \le 11,$
indices	$-12 \le k \le 12,$
	$-13 \le l \le 13$
Reflections collected	7271
Number of independent	
reflections	3375
R <sub>int</sub>	0.0217
Number of reflection with $I > 2\sigma(I)$	2096
<i>R</i> -factors on $I \ge 2\sigma(I)$	
$R_1$	0.0354
$wR_2$	0.0763
<i>R</i> -factors (on all reflections)	
$R_1$	0.0568
$wR_2$	0.0788
Q-factor on $F^2$	1.001
Residual electron	0.040 / 0.1/7
density, $\rho_{min}/\rho_{max}$ , e A <sup>3</sup>	-0.240 / 0.167

SHELXS–97 and SHELXL-97 programs.<sup>16</sup> Hydrogen atoms were placed in geometrically calculated positions and they were included in the refinement using a riding model with dependent thermal parameters. The experimental X-ray diffraction data (Table 1) were deposited with the Cambridge Structural Database (CCDC 1033803).

## **Results and Discussion**

In order to carry out comparison studies of the photochemical and photophysical behavior of (E)-2-styrylquinazolin-4(3*H*)-ones in solutions, a series of derivatives **3a**-d (Scheme 1) was synthesized. The C=C bond formation techniques in (het)arylstilbenes often have a specific nature, while the condensation of 2-methylazines with aromatic aldehydes in the presence of zinc chloride or sodium acetate does not always ensure a high yield of the target compounds.<sup>4</sup> The use of boric acid as a catalyst in the final stage of the synthesis, the condensation of 2-methyl-3-phenylquinazolin-4(3H)-one (1a) with aromatic aldehydes 2a-d, allowed us to obtain various diazinones 3a-d and, most importantly, their hydroxy derivatives in high yields.



Reagents and conditions: *i*. (MeCO)<sub>2</sub>O; *ii*. R-NH<sub>2</sub>, C<sub>5</sub>H<sub>5</sub>N, P<sub>2</sub>O<sub>5</sub>,  $\Delta$ ; *iii*. R<sup>1</sup>-CHO (2a-d), MeCOOH, H<sub>3</sub>BO<sub>3</sub>,  $\Delta$ .

Photoinduced transformations of (E)-2-styrylquinazolin-4(3*H*)-ones 3a-d in neutral media were studied and some regularities were identified using absorption and NMR spectroscopy. Thus, the presence of a hydroxy group (compounds 3c,d) and/or an annulated aromatic fragment (compounds 3b,d) in the (E)-2-styrylquinazolin-4(3H)one molecules leads to a bathochromic shift of the absorption band maximum to the 290-450 nm range (Fig. 1) in the electron absorption spectra of their solutions. Fluorescence with an emission maximum at 428 nm ( $\lambda_{ex} = 343$  nm) (see Fig. 1, a; Table 2) can be seen in the emission spectra of compound 3a. When going to hydroxy derivative 3c, the radiation intensity considerably decreases. For naphthyl derivatives the opposite is true (see Fig. 1), namely an increase in the intensity of the long wavelength emission band in the wavelength region of 350-550 nm when going from compound **3b** to **3d**. Thus, the emission ability of (E)-2-styrylquinazolin-4(3H)-ones in this region does not depend directly on the presence of the OH group, which normally quenches the luminescence of fluorophores.<sup>1</sup>

A tendency of (E)-2-styrylquinazolin-4(3*H*)-ones in a solution to transform photochemically when being exposed to ultraviolet light of a DRSh-250 lamp (an UFC-6 light filter) was confirmed by a decrease of the long wavelength absorption band intensity in their UV spectra to a specific unchangeable level (Fig. 2, Table 2). At that, considerable temporal differences of photochemical transformations in solutions of compounds **3a**,**d** and **3b**,**c** were observed. For isomers E-**3a**,**d**, possessing fluorescence in the 350—550 nm range, this time period was larger by one or two orders of magnitude (see Table 1), which indicates an interrelation between the emission ability of styrylquinazolinones and the rate of their photochemical transformations in solutions.

The formation of the photosteady state in solutions of (het)arylstilbenes is generally related to a reversible photoisomerization of the -C=C- bond, which is induced by light in the 350-450 nm wavelength range. The presence of isobestic points in the absorption spectra of the exposed solutions of compounds *E*-**3** (see Fig. 2) can be an indication of the emergence of such a photosteady state in these solutions. However, the decrease in the intensity of the long wavelength absorption band in the UV spectra can also be a result of competing processes (of [2 + 2]-cycloaddition type), also related to photochemical transformations of the -C=C- bond. The questions about the nature of the photosteady state of the system, about the photoproducts and their ratio were answered using NMR spectroscopy.

According to the <sup>1</sup>H NMR spectra of the exposed solutions of E-**3a**-c (3·10<sup>-2</sup> mol L<sup>-1</sup>) in DMSO-d<sub>6</sub>, the photoinduced products of E-Z-isomerization and [2+2]cycloaddition are the main ones, but there are some differences in the priorities of the processes taking place. Thus, the photoinduced E-Z-isomerization is characteristic of the molecules of compound E-3c. In the process of exposure of solutions of E-3c in DMSO-d<sub>6</sub> after 2 h the ratio of isomers E-3c to Z-3c reached 16 to 84%, respectively. In the next 30 h of exposure the equilibrium in the solution was retained with little change of the Z-form content (within 84-88%). The formation of the Z-isomer was confirmed by the presence of doublets of vicinal protons of the C=C bond in the  $\delta$  5.9–6.7 region with the spin-spin coupling constant of 12.4 Hz in the <sup>1</sup>H NMR spectra of the exposed solution of compound 3c. Consequently, in the case of isomer E-3c, a photosteady equilibrium is said to be established in solutions under these conditions.

In the case of photochemical transformation of *E*-isomers **3a**,**b** in solutions against the background of the equilibrium mixture of *E*- and *Z*-isomers formed in the first several hours upon long exposure, there was a gradual appearance of a photodimerization product. In the <sup>1</sup>H NMR spectra of the exposed solution of **3a**,**b** in DMSO-d<sub>6</sub> this is evidenced by the proton signals of the photoproduct cyclobutane ring as a characteristic<sup>17</sup> AA'BB' spin system in the  $\delta$  4.0–5.0 region (Fig. 3). Apparently, the high concentration of reagents in the exposed solutions in DMSO-d<sub>6</sub> and the absence of the *ortho*-substituent in their styryl fragment facilitates the [2 + 2]-photocycloaddition reaction of quinazolin-4(3*H*)-ones. On the whole, after



Fig. 1. Electron absorption spectra (1), excitation spectra (2), and fluorescence emission spectra (3) of compounds E-3a (a), E-3b (b), E-3c (c), and E-3d (d) (2  $\cdot$  10<sup>-5</sup> mol L<sup>-1</sup>, in *n*-butanol, the optical pathlength is 10 mm). The excitation and emission wavelengths,  $\lambda$ /nm: 343 and 428 (a); 286 and 426 (b, c); 336 and 430 (d), respectively.



**Fig. 2.** (*a*) The changes in the electron absorption spectra of a solution of compound **3c**  $(2 \cdot 10^{-5} \text{ mol } \text{L}^{-1}, \text{ acetonitrile})$  in the process of *E*-*Z*-photoisomerization: *I* is the spectrum of the starting *E*-isomer, *2* is the spectrum of the photosteady mixture with the *Z*-isomer. (*b*) Kinetic curves of the dependence of the change in optical density (the ratio of the measured optical density to the optical density of the *E*-isomer, *A*/*A<sub>E</sub>*) at  $\lambda = 350$  nm of the photosteady solution with *Z*-**3c**  $(2 \cdot 10^{-5} \text{ mol } \text{L}^{-1}, \text{ acetonitrile})$  on the heating time at 35 (*I*), 55 (*2*), 65 (*3*), 75 °C (*4*).

Compound	Solvent	$\frac{\lambda_{\rm fl}{}^a/\rm nm}{(\Phi_{\rm rel}{}^b(\%))}$	$\lambda_{\max}^{c/1}$	t <sup>d</sup> /s	
			Starting <i>E</i> -isomer	Reaction mixture	
<b>3</b> a	<i>n</i> -Butanol	428 (0.15)	335 (21050)	325 (15200)	1140
	Acetonitrile	_	350 (22400)	325 (13550)	4620
	DMF	_	338 (20300)	337 (18550)	>1200
3b	n-Butanol	426 ()	355 (20150)	355 (6250)	14
	Acetonitrile	_	350 (21150)	350 (10550)	16
	DMF	_	355 (16550)	355 (8650)	14
3c	n-Butanol	426 ()	358 (18500)	358 (5250)	16
	Acetonitrile	_	350 (21150)	350 (9550)	16
	DMF	_	358 (20100)	358 (9950)	16
3d	n-Butanol	430 (0.2)	389 (20000)	407 (2350)	690
	DMF	_	385 (21260)	407 (2450)	1080

Table 2. Photophysical and photochemical characteristics of styrylquinazolinones E-3a-d

<sup>*a*</sup> The long wavelength luminescence maximum.

<sup>b</sup> Relative quantum yield of the long wavelength luminescence of E-isomers.

<sup>c</sup> The absorption maxima and the corresponding extinction coefficients<sup>11</sup> (L mol<sup>-1</sup> cm<sup>-1</sup>) of styrylquinazolinones **3** (2  $\cdot$  10<sup>-5</sup> mol L<sup>-1</sup>).

<sup>d</sup> Duration of photochemical reactions of solutions upon exposure to irradiation.

30 h of exposure the Z-form (33% for compound **3a**, 58% for compound **3b**) and the photodimerization product (7–10%) were observed in the reaction mixture, along with the *E*-isomer.

The analysis of the <sup>1</sup>H NMR spectra of the exposed solution of isomer *E*-**3d** in DMSO-d<sub>6</sub> showed that in this case the photoproducts differ from those synthesized at the photochemical transformation of molecules **3a**-**c** by the absence of *E*-, *Z*-isomers and cyclobutane-containing adducts. After chromatographic separation, the three main photoproducts were characterized by EI mass spectra. The analysis of the molecular ion peaks of the composition  $[C_{26}H_{18}N_2O_2]$  with *m/z* 390 (**4a**),  $[C_{26}H_{16}N_2O_2]$  with *m/z* 388 (**4b**), and  $[C_{14}H_{10}N_2O]$  with *m/z* 222 (**4c**) allows us to assign the synthesized structures to spironaphthopyran **4a** and the products of its rearrangement and decomposition **4b,c** (Scheme 2).

Stilbens, as it is known,<sup>18</sup> tend to reversibly photo and/or thermally Z—E-isomerize. In our studies of <sup>1</sup>H NMR and

UV spectral data of the reaction mixtures of compounds **3a,b** upon prolonged keeping in dark or heating of the solutions without exposure to light, no changes in the ratio of *E*- and *Z*-isomers were observed. On the contrary, the studies of the photosteady solutions of **3c** by NMR indicated a reversible isomerization of the *Z*-form in the dark. When the exposed solutions with *Z*-**3c** as a major component was allowed to stand in dark for 2–3 days, the equilibrium shifted in the direction of the starting isomer *E*-**3c**. In turn, heating of *Z*-**3c** solutions in DMSO-d<sub>6</sub> for 4 h (105–110 °C) also led to a complete transformation of the latter into the *E*-form.

Using UV spectroscopy, additional confirmation of the thermal Z—E-inversion of compound **3c** was obtained. In the UV spectra of the acetonitrile photosteady solutions of compound Z-**3c**, the dark Z—E-isomerization was accompanied by a gradual increase of the long wavelength absorption maximum in the 350 nm range until the formation of the absorption spectrum characteristic of the starting E-isomer (see Fig. 2). Kinetic studies of the depend-



Fig. 3. <sup>1</sup>H NMR spectra (400 MHz) of compound 3a in DMSO-d<sub>6</sub> ( $3 \cdot 10^{-2}$  mol L<sup>-1</sup>) before (1) and after 32 h of irradiation (2).



0

4c

ence of the Z–E-inversion of compound **3c** on temperature based on UV spectral data demonstrate an acceleration of the reaction from 28 h for solutions thermostated at 35 °C to 40 min at 75 °C (see Fig. 2, b). Several cycles of photo/thermal E-Z-E-isomerization under these conditions demonstrated the stability of the conjugated system of compound **3c** to destruction and side transformations. Since the duration of photo E-Z- and dark Z-Eisomerization for compound **3c** differs by two orders of magnitude and the photoisomerization reaction is significantly shifted in the direction of the Z-form, we can conclude that the electron absorption spectrum of the photosteady solution of **3c** is very similar to the spectrum of the Z-isomer (see Table 2, Fig. 2, a).

Thus, as a result of exposure, ortho-hydroxystyrylquinazolinones 3 in a solution demonstrates two types of transformations (see Scheme 2), related to reversible E-Z-(in the case of **3c**) and valence isomerization (in the case of 3d). Clearly, the choice of one of two possible competing mechanisms is determined not only by the properties of the electron structure of the ortho-hydroxystyryl fragment, but also by the spatial position relative to the diazinone core. Thus, according to the X-ray diffraction studies (see Fig. 4), the molecule E-3c has a practically planar styrylquinazolinone conjugation system, where the angle between the mean square planes passing the (het)aryl fragments C(1)N(1)C(2)C(3)C(8)N(2) and C(17)C(18)C(19)C(20)C(21)C(22) is 14.72°. The modules of the torsion angles in the conjugated ethylene fragment N(2)C(1)C(15)C(16) and C(15)C(16)C(17)C(18) are 12.41° and 27.42°, respectively. The phenyl substituent at the N(1) atom of the diazinone ring (see Fig. 4) is turned relative to the conjugation plane of the chromophoric core. The angle between the mean square planes passing N(2)C(1)N(1)C(2)C(3)C(8) and

C(9)C(10)C(11)C(12)C(13)C(14) is 70.25°. The ethylene fragment with *trans*-configuration is stabilized in "pseudocisoid" conformation relative to the -N=C- bond of the heterocycle, while the hydroxy group of the styryl moiety is turned in the direction of the N(2) atom of the heterocycle. The C-C bond lengths of the ethylene bridge C(1)-C(15)=C(16)-C(17) are equal to 1.459(2), 1.325(2), and 1.460(2) Å, respectively. Such a lengthening of C-C single bonds can ease the conformational trans-formations of terminal groups in this fragment in solutions.

Indeed, according to the NMR data in solutions the conjugated system in molecules E-3c breaks down as a result of a considerable turn of the 2-hydroxyphenyl substituent around the C–C single bond relative to the ethenylquinazolinone framework. This is evidenced by the cross peaks of practically equal intensities between  $H(\alpha)$ ,  $H(\beta)$  and each of the protons of the H(20) and OH group of the styryl fragment in the 2D <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of compound E-3c in DMSO-d<sub>6</sub>. A selected correlation of protons is shown in Scheme 2. At the same time, the "pseudocisoid" (relative to the C=N bond) conformation and the conjugation of the ethylene fragment with the heterocycle are retained, which is evidenced by the strong cross peaks between the  $H(\alpha)$  atom and the spatially close to it ortho-protons H(10) and H(14) of the phenyl substituent. Thus, the turn of the 2-hydroxyphenyl moiety from the plane of conjugation of the ethenylhetaryl core in molecules E-3c is the reason of the activation of the -CH=CH- bond, the acceleration of photochemical E-Z-isomerization proceeding by the rotational mechanism,<sup>18</sup> and the luminescence quenching in the 350-550 nm range (see Fig. 1, c). The mechanism of thermal Z-Einversion of compound **3c** (see Scheme 2), in turn, can be related either to the double tautomeric transformation through the quinonoid form during the reversible transfer



**Fig. 4.** (*a*) The molecular structure of compound E-**3c** based on X-ray diffraction studies (thermal ellipsoids are given with 50% probability). (*b*) Molecular packing, formed by centrosymmetric dimers with intermolecularly close photosensitive C=C groups at a distance of 4.7 Å and stabilized by intermolecular hydrogen bonds (O(2)…H(1)O(1) 1.78 Å).

of the OH group proton to the N(1) atom of the heterocycle, located close in space, or to the formation of the spiropyrane intermediate. The absence of characteristic proton signals of the spirobenzopyrane adduct<sup>19</sup> in the region  $\delta$  4.5–6 in the <sup>1</sup>H NMR spectra of the reaction mixture of Z- and E-isomers indicates that the former mechanism is preferred.

In compound E-3d, according to the cross peaks between the H( $\alpha$ ) atom and the spatially close *ortho*-protons H(10) and H(14) of the phenyl substituent in the 2D  $^{1}H$ – $^{1}H$ NOESY spectra, the isomer molecules in a solution have a "pseudocisoid" conformation of the ethylene fragment similar to E-3c (see Scheme 2). At the same time, a considerable increase in the intensity of the cross peak between protons H(22) and H( $\beta$ ) of the naphthyl moiety as compared to that of protons H(22) and H( $\alpha$ ) indicates a conjugation of this fragment with the ethenylhetaryl core of E-3d. This is confirmed by broad luminescence band in the 350-550 nm range in the emission spectra of solutions of E-3d (see Fig. 1, d). In addition, in experiments using a mercury lamp of medium pressure (100 W) the decrease in intensity of the luminous flux of the emitter leads to a discontinuation of the photochemical transformations of molecule *E*-3d in solutions (unlike *E*-3a-c). In <sup>1</sup>H NMR spectra of the exposed solutions, only signals of E-isomer were present. Consequently, the stabilization in solutions of the flattened chromophore structure not only contributes to the appearance of noticeable luminescence, and, consequently, to the decrease of the rate of the photochemical transformations of molecule E-3d, but also assumes a mechanism of isomerization of the -C=Cbond different from the one which takes place for compound E-3c. Apparently, the photochemical transformation is caused by the appearance of the ST-state during charge transfer<sup>11</sup> from the donor (naphthyl fragment) to the acceptor (diazinone fragment) part of the excited chromophoric molecular system. At that, the conformational turn around the  $-C(\alpha)-C(\beta)$  bond of terminal groups can be caused by the formation of the intermediate A in the course of the tautomeric transformations (see Scheme 2). Further photochemical transformations of the excited molecule E-3d probably can proceed through both the intermediate C (ionic mechanism), and the intermediate **B** in the course of the photochemically allowed electrocyclic reaction.<sup>19,20</sup>

When studying the influence of the medium pH on the photophysical properties of quinazolinones, no changes in the photoinduced behavior of compounds **3a,b** upon the addition of CH<sub>3</sub>COOH or Bu<sup>t</sup>OK (pH 3–4 and 8–12) were observed. For hydroxy derivatives **3c,d**, on the other hand, this influence was considerable. Moderate acceleration of the E–Z-isomerization of compound **3c** was observed in acidic media (CH<sub>3</sub>COOH, pH 3–4). Spectrophotometric titration of solutions of diazinones **3c,d** with strong bases Me<sub>4</sub>NOH or Bu<sup>t</sup>OK (Fig. 5, Table 3) was

![](_page_8_Figure_4.jpeg)

**Fig. 5.** (*a*) The changes in the electron absorption spectra of solutions of compound E-**3c**  $(2 \cdot 10^{-5} \text{ mol } \text{L}^{-1}, \text{ DMF})$  in the course of UV spectrophotometric titration with Me<sub>4</sub>NOH (the change in the concentration of **3c** : Me<sub>4</sub>NOH in molar ratio from 1 : 0 to 1 : 20). (*b*) Electron absorption spectra (*1*), excitation spectra (*2*), and fluorescence emission spectra (*3*) of the quinonoid form of **3c**  $(2 \cdot 10^{-5} \text{ mol } \text{L}^{-1})$  in DMF (optical pathlength 10 mm, excitation and emission wavelength,  $\lambda/\text{nm}$ : 512 and 606, respectively).

**Table 3.** Selected photophysical characteristics of the quinonoid form of 3c,d (2 · 10<sup>-5</sup> mol L<sup>-1</sup>) in basic media (Me<sub>4</sub>NOH or Bu<sup>t</sup>OK)

Com-	Solvent	$C_{E-3}$ : $C_{base}^{a}$	$\lambda_{ex}$	$\lambda_{em}$	$\Delta v^b$	$\Phi_{\rm rel}$
pound			n	m	/cm	(70)
3c	n-Butanol	1:20	450	600	5556	5.6
	Acetonitrile	1:20	486	604	4020	5.9
	DMF	1:20	512	606	3029	12.5
3d	<i>n</i> -Butanol	1:12	468	580	4126	0.18
	DMF	1:12	548	595	1441	0.63

<sup>a</sup> The molar ratio of concentrations.

<sup>b</sup> Stokes shift.

accompanied by a decrease of the light absorption maximum in the  $\lambda_{max}$  369 nm and 387 nm range and an appearance of a long wavelength band at 520 and 548 nm (for **3c** and **3d**, respectively) in their electron absorption spectra. The change of the solution color from pale yellow to crimson orange was accompanied by an appearance of noticeable broadband luminescence in the visible region with a maximum at 580–607 nm (see Fig. 5). At that, the influence of the solvent nature on the long wavelength emission band intensity, the Stokes shift, and the relative quantum yields of the studied compounds were noted (see Table 3).

Such a considerable change in the spectral properties of compounds 3c,d are related not only to the formation of the anionic forms as a result of a CTC-transition<sup>11</sup> in the intermolecular complex, but also to a significant redistribution of electron density in the chromophore conjugation system itself. The tautomeric transformations in the course of titration of solutions of **3c**,**d** in DMSO-d<sub>6</sub> with bases were confirmed by the changes in the chemical shifts of protons in the <sup>1</sup>H NMR spectra (Fig. 6). The presence of several sets of proton signals with the spin-spin coupling constants of vicinal protons  $H(\alpha)$  and  $H(\beta)$  varying in the 14.6-16.2 Hz range in the spectra, indicated the stabilization of possible intermediates of type A, B, and C (Scheme 3) with the transoid<sup>21</sup> conformation of the =CH( $\alpha$ )-CH( $\beta$ )= fragment. In strongly basic media, the equilibrium is completely shifted in the direction of one of the conformers of the suggested intermediate C, which is indicated by the comparison of the results of spectrophotometric titration of compounds 3c,d and the corresponding <sup>1</sup>H and <sup>13</sup>C NMR spectra (see Fig. 6). In the

![](_page_9_Figure_4.jpeg)

**Fig. 6.** (a) <sup>1</sup>H NMR spectra (400 MHz) of the titration of a solution of *E*-**3c** in DMSO-d<sub>6</sub> ( $3 \cdot 10^{-2}$  mol L<sup>-1</sup>) upon the addition of Me<sub>4</sub>NOH in the molar ratio of 1 : 0 (*I*), 1 : 5 (*2*), 1 : 10 (*3*), 1 : 15 (*4*). (*b*) <sup>13</sup>C NMR spectra (125.76 MHz) of solutions in DMSO-d<sub>6</sub> of compounds *E*-**3c** ( $3 \cdot 10^{-2}$  mol L<sup>-1</sup>, DMF) (*I*) and *E*-**3c** : Me<sub>4</sub>NOH in the molar ratio of 1 : 20 (*2*).

![](_page_9_Figure_6.jpeg)

<sup>13</sup>C NMR spectra of compound **3c**, the quinonoid structure<sup>22</sup> of the aryl moiety of isomer C was confirmed by a considerable downfield shift of the carbon atom C(16) signal to  $\delta$  172.02 (see Fig. 6). In turn, the transfer of the negative charge to the oxygen atom of the acceptor quinazoline core of the tautomer might be quite responsible for the shift of the carbon atoms C(4) and C(9) signals to  $\delta$  170.07 and 151.56 of the low field, respectively. The probability of charge transfer to the mentioned oxygen atom of the heterocycle is partly confirmed by the shortened (1.78 Å) intermolecular hydrogen bonds in crystals *E*-**3c**, as shown by X-ray diffraction studies (see Fig. 4).

In the case of compound E-3c, an increase of the concentration of the base in solutions leads to a shift of the equilibrium from the photochemical processes of isomerization to luminescence. In the course of titration of solutions of 3c in DMSO-d<sub>6</sub> with Bu<sup>t</sup>OK followed by irradiation, the ratio of Z- and E-isomers were found to change with an increase of the latter based on <sup>1</sup>H NMR data.

In conclusion, using compound *E*-3c as an example, we demonstrated the ability of ortho-hydroxystyrylquinazolinones to reversible photo/thermal switch in solutions. The process of E-Z-isomerization is initiated by light in the 300-400 nm range, the reverse Z-E-inversion is a dark process and significantly accelerates at elevated temperatures. Using X-ray diffraction analysis and NMR spectroscopy the differences in the spatial organization of the *ortho*-hydroxystyryldiazinone system of *E*-3c,d in crystals and in solutions related to the turn of the aryl moiety were determined. We showed the influence of the conformation on the equilibrium shift in the direction of either the photochemical or luminescence process. Taking into account this factor and the ability to undergo tautomeric transformations of the chromophoric core of ortho-hydroxystyrylquinazolinones, we suggest two mechanisms of photoinduced isomerization of the disubstituted ethylene fragment: the rotational mechanism<sup>18</sup> (for molecules E-3c) and the mechanism (for molecules E-3d) induced by the excited ST-state.<sup>11</sup> We determine the interrelation of the effects of a strong base, the nature of the solvent and the luminescence intensity of solutions of E-3c,d, the formation of the charge transfer complex being accompanied by the tautomeric transformation of the conjugated system into the quinonoid form. It was shown that the photochromic and luminescent properties of such compounds can be regulated by changing the pH of the medium.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 14-03-00340).

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Received February 7, 2014; in revised form July 17, 2014