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Synthesis, absorption and fluorescence of hydrazone colorants based on pyrrolinone esters

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ABSTRACT

Ten azo dyes were prepared by diazotization of a series of electronically different *para* substituted anilines and subsequent azo coupling of these diazonium salts with ethyl 4,5-dihydro-5-oxo-2-aryl(1H) pyrrole-3-carboxylate as a the coupling component. All of the dyes were confirmed as keto-hydrazone tautomers and were found as a mixtures of *E*- and *Z*-isomers with respect to the exocyclic C=N bond by ^{1}H-NMR spectroscopy. The absorption spectra are all similar irrespective of substituent and solvent. By comparison the fluorescence is strongly dependent on the electronic character of the substituents. All compounds fluoresce in a low temperature solvent glass and in the solid state and only the 4-cyanophenyl and 4-nitrophenyl derivatives show fluorescence in solution at room temperature. The spectroscopic behavior is explained in terms of competition between *E*/*Z* isomerization and fluorescence after excitation.

1. Introduction

Azo compounds are by far the largest group of commercial organic dyes and pigments [1,2]. Their synthesis is economically attractive; usually a two-step sequence of diazonium salt formation from either an aromatic or heteroaromatic primary amine which reacts with a wide choice of coupling components, usually amino- and hydroxy-substituted (hetero)aromatics or enolizable (di) ketones. The products of coupling components with the latter two types of passive components can be formally called hydroxy-azo compounds, which may immediately undergo a proton transfer from oxygen to more distant nitrogen, followed by reordering of single and double bonds forming a keto-hydrazone tautomer. An equilibrium between both tautomers in solution depends mainly on the type of coupling component, on the character of substituents on both parts of the molecule and sometimes even on either the environment or the temperature. Azo dyes derived from frequently used enols e.g. 3-substituted 1-phenylpyrazol-5-ones are found exclusively as the keto-hydrazone tautomers [3,4].

Azo tautomers arise from a reaction usually with an *E*-configuration of an exocyclic N=N bond and *Z* isomers can be obtained by a photochemical *E*/*Z* isomerization [5]. Hydrazone tautomers are usually arranged in a form enabling intramolecular hydrogen bonding between oxygen and nitrogen atoms taking part in the formal tautomeric proton transfer, thus forming a *Z*-arrangement of the exocyclic C=N bond. Such a configuration in the solid state was experimentally confirmed by X-ray diffractometry for β-naphthol based hydrazones [6] or a pyrazoline hydrazone [7], which is probably the structurally closest compound with respect to the pyrrolinone hydrazones investigated in this presented study.

The absorption spectra of hydrazones are generally bathochromatically shifted with respect to corresponding azo tautomers; the effect of polar substituents on absorption maxima is mutually opposite [8,9]. Hydrazone tautomers quite often fluoresce, e.g. the derivatives of pyrazolone hydrazones [10]. Only hydrazone fluorescence was observed in the case, where both tautomers were present, and thus excited state intramolecular proton transfer process (from oxygen to nitrogen) was detected by comparison of absorption and fluorescence excitation spectra [11].

Ethyl 4,5-dihydro-5-oxo-2-phenyl(1H)pyrrole-3-carboxylate (phenyl pyrrolinone ester **1**) has become an interesting intermediate in the colorant chemistry in recent years. The

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Table 1
Structure of prepared dyes.

Dye	Ar	R	Dye	Ar	R
1a	Phenyl	H	**2a**	2-naphthyl	H
1b	Phenyl	4-CN	**2b**	2-naphthyl	4-CN
1c	Phenyl	4-NO_2	**2c**	2-naphthyl	4-NO_2
1d	Phenyl	4-OH	**2d**	2-naphthyl	4-OH
1e	Phenyl	4-MeO	**2e**	2-naphthyl	4-MeO

methylene carbon in position 4 is activated by carbonyl and ester groups and a condensation with aldehydes [12,13], esters [14] and a reaction with aromatic nitriles [15–17] can be carried out. The products of an azo coupling reaction between pyrrolinone ester **1** and diazotized aromatic amines were first described in a patent in 2001 [18]. Since this patent only contains a few examples of the derived dyes without detailed spectral data and as we are generally interested in the dyes from pyrrolinone esters, it was decided to investigate these compounds in detail. First of all the unsubstituted ^{15}N-labeled ethyl 5-oxo-2-phenyl-4-(2-phenylhydrazono)-4,5-dihydro-^{1}H-pyrrole-3-carboxylate (compound **1a** in Table 1) was synthesized according to Scheme 1 [19]. The product was formed as a hydrazone tautomer as confirmed by ^{13}C and ^{15}N chemical shifts, and was obtained as a mixture of *E* and *Z* isomers according to ^{n}J(^{15}N, ^{13}C) coupling constants. A comparison of the ^{1}H-NMR chemical shifts with GIAO DFT calculations enabled determination of a distinct configuration of the carboxy ester group in both isomers.

Here we present the syntheses of a representative set of ten derivatives (Table 1) from the azo coupling of diazotized *para* substituted anilines with phenyl and 2-naphthyl pyrrolinone ester **1**, **2** (Scheme 1). Their tautomeric form was estimated by NMR spectroscopy. The dependence of their absorption spectra on the character of the substituents was studied together with their fluorescence ability in various environments.

2. Experimental

2.1. Instrumental equipment

N-Methylpyrrolidinone (NMP), dioxane, dimethyl sulfoxide (DMSO), acetonitrile and acetone (all of spectroscopic grade) were purchased from Fluka and used for room temperature spectroscopic measurements.

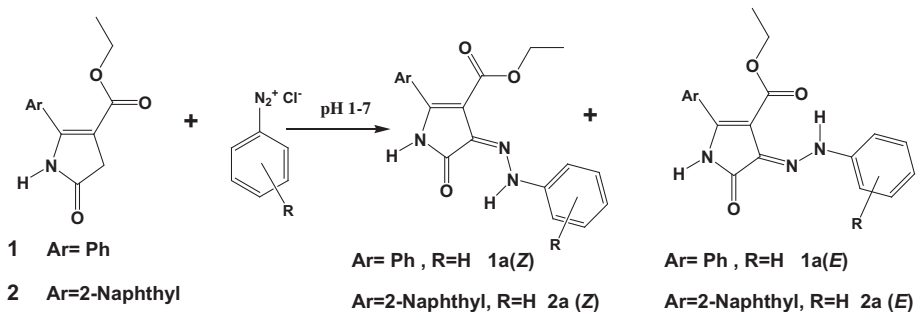
The absorption spectra were recorded using a Perkin–Elmer Lambda 35 spectrophotometer in 1 cm pathlength quartz cuvettes. Photochemical isomerization was also monitored by absorption spectroscopy. The dye solutions in NMP were prepared in the dark at concentrations 1×10^{-5} mol/L and the measurements of absorbance were recorded before and after irradiation by daylight for 10 h.

A Perkin-Elmer (P.-E.) LS55 was used for measuring fluorescence spectra at room and low temperatures. Methyltetrahydrofuran (MTHF) was used as a solvent to create an organic frozen glass to measure low temperature fluorescence spectra using a commercial low temperature accessory also from P.-E. This accessory also from P.-E. contains an isolated box filled by liquid nitrogen and the measurements are carried out in a round cuvette (diameter about 1 mm). The solid-state luminescence spectra were recorded also on the same instrument equipped with a P.-E. accessory for solid-state measurements. Polycrystalline samples were placed under quartz plate and the emission spectra were recorded using front face geometry. The fluorescence quantum yields in solution (φ_F) were determined using 4-dicyanomethylene-2-methyl-6-[*p*(dimethylamino)styryl]-4H-pyran (DCM) ($\varphi_F = 0.57$, $\lambda_{max} = 520$ nm) in 1-propanol as the standard [20].

An EA 1108 FISONS instrument was used for elemental analysis. Melting points of compounds were checked on a Büchi 510 melting point apparatus. Thin-layer chromatography (TLC) was performed by a Kieselgel 60 F254 (Merck, Darmstadt, Germany), for observation of reaction progress and the purity of the prepared intermediates and dyes.

Positive-ion and negative-ion atmospheric pressure chemical ionization (APCI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* 50–1000. The samples were dissolved in acetonitrile and analyzed by direct infusion at the flow rate 100 μL min^{-1}. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: the isolation width *m*/*z* = 4, the collision amplitude in the range 0.7–1.0 V depending on the precursor ion stability, the temperature of drying gas was 330 °C, the APCI temperature was 400 °C, the tuning parameter compound stability was 100%, the flow rate and the pressure of nitrogen were 4 L min^{-1} and 45 psi, respectively.

Chromatographic apparatus consisted of an LC 1100 Series (Agilent Technologies, USA) and the ion trap mass spectrometer MSD TRAP XCT Plus system (Agilent Technologies, USA) equipped with ESI and APCI probes was used. Negative-ion ESI mass spectra were recorded in mass range 50–1500 Da in all experiments. The ion trap analyzer was tuned to obtain an optimal response in the range of expected *m*/*z* values (target mass was set to *m*/*z* = 500). Another ESI ion source parameters were as follows: drying gas flow 8 L min^{-1}, nebulizer gas pressure 40 psi, drying gas. Samples were dissolved in methanol in appropriate concentrations for MS detection. Injection volumes of 20 μL, a flow-rate of 0.2 mL min^{-1} and column temperature of 30 °C were used in all analysis. The separation was performed in following chromatographic system: An octadecyl silica cartridge column, Zorbax Eclipse XDB C_{18} (150 × 2.1 mm i.d., 5 μm particle size) purchased from Agilent



Scheme 1. Syntheses of the studied compounds.

(HPST Prague, Czech Republic) was used for the separation of samples. Gradient was employed, with 20 m*M* ammonium acetate in water as solvent A (pH 4) and acetonitrile as solvent B: from 5% B in 0–3 min, then 5–100% in 3–20 min to 100% B in 20–30 min.

The ^{1}H-NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400.13 MHz). The samples were dissolved in hexadeuteriodimethyl sulfoxide. The ^{1}H chemical shifts were referenced to the central signal of the solvent ($\delta = 2.55$).

2.2. Synthesis

Starting pyrrolinone esters, ethyl 4,5-dihydro-5-oxo-2-phenyl(1H)pyrrole-3-carboxylate (**1**) and ethyl-4,5-dihydro-5-oxo-2-naphthyl(1H)pyrrole-3-carboxylate (**2**), were synthesized according to published procedures [13,17].

4-Aminophenol, 4-nitroaniline and 4-cyanoaniline were all purchased from Aldrich Chemical Company.

All ten dyes were prepared by diazotization of the primary aromatic amines followed by a coupling reaction. The aromatic amine (10 mmol), concentrated HCl (35%, 4 mL) and water (30 mL) were stirred until amine was completely dissolved. Then the mixture was cooled (external cooling) at the temperature 0–5 °C and $NaNO_2$ (10 mL of 1M solution) were dropwise added during 30 min. When the reaction was completed, the solution of the diazonium compound was used for the next coupling reaction.

Pyrrolinone ester intermediate (10 mmol) was dissolved in methanol (100 mL) by heating, the mixture was externally cooled to 0 °C and the solution of diazonium salt was added dropwise. The reaction mixture was stirred at 0–5 °C for 4 h while warming gradually to room temperature and then stirred overnight. The precipitated dye was filtered off and washed with methanol and water. Final products were recrystallized, characterized by elemental analysis, mass spectrometry and melting points, which together with reaction yields are presented in the following text. Data from ^{1}H NMR spectroscopy are presented in section 3.1.

2.3. Ethyl 5-oxo-2-phenyl-4-(2-phenylhydrazono)-4,5-dihydro-1H-pyrrole-3-carboxylate (*1a*)

Preparative yield 63%; purified by recrystallization from ethanol, mp = 193–195 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.25 (3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.20 (2H, q, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.08–7.66 (10H, m, aromatic protons); 11.40 (1H, br. s,–CONH–); 13.10 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.92 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.09 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.08–7.66 (10H, m, aromatic protons); 11.31 (1H, br. s,–CONH–); 13.01 (1H, br. s, –NHN=).

MS analysis, *M* = 335. Positive-ion MS: *m*/*z* 336 $[M + H]^+$, 100%; *m*/*z* 290 $[M + H–C_2H_5OH]^+$, Negative-ion MS: *m*/*z* 334 $[M - H]^-$, 100%; *m*/*z* 288 $[M - H–C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{19}H_{17}N_3O_3$): C(68.05%), H(5.11%), N(12.53%). Found: C (68.10%), H(5.28%), N(12.63%).

2.4. Ethyl 5-oxo-2-phenyl-4-[2-(4-Cyanophenyl)hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (*1b*)

Preparative yield 56%; purified by recrystallization from ethanol, mp = 234–236 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.23 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz CH_3); 4.19 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.37–7.85 (9H, m, aromatic protons); 11.49 (1H, br. s,–CONH–); 13.15 (1H, br. s, –NHN=).

Table 2
^{1}H chemical shifts in *Z* and *E* isomers of the dyes **1a-e** and **2a-e** measured in hexadeuteriodimethyl sulfoxide.

Compound	^{1}H Chemicalshift (ppm)				
	–NHN=	–CONH–	OCH_2CH_3	Aromatic protons	%
1a (*Z*)	13.10	11.40	4.20, 1.25	7.08–7.66	62
(*E*)	13.01	11.31	4.09, 0.92		38
1b (*Z*)	13.15	11.49	4.19, 1.23	7.37–7.85	55
(*E*)	13.01	11.43	4.08, 0.91		45
1c (*Z*)	13.10	11.52	4.20, 1.24	7.39–8.30	62
(*E*)	13.31	11.52	4.09, 0.92		38
1d (*Z*)[a]	13.18	11.32	4.19, 1.23	6.80–7.63	69
(*E*)[a]	12.97	11.20	4.06, 0.89		31
1e (*Z*)[b]	13.14	11.35	4.20, 1.24	7.01–7.65	80
(*E*)[c]	13.00	11.24	4.08, 0.91		20
2a (*Z*)	13.15	11.53	4.22, 1.21	7.09–8.22	70
(*E*)	13.06	11.42	4.09, 0.82		30
2b (*Z*)	13.05	11.63	4.21, 1.20	7.39–8.26	71
(*E*)	13.20	11.56	4.09, 0.82		29
2c (*Z*)	13.16	11.63	4.22, 1.21	7.42–8.32	60
(*E*)	13.32	11.63	4.10, 0.84		40
2d (*Z*)[d]	13.26	11.45	4.21, 1.21	6.84–8.22	85
(*E*)[e]	13.03	11.32	4.07, 0.82		15
2e (*Z*)[f]	13.22	11.47	4.21, 1.22	7.00–8.22	75
(*E*)[g]	13.04	11.35	4.08, 0.82		25

[a] 10.80 (OH) broadened signal.
[b] 3.80 (OCH_3).
[c] 3.79 (OCH_3).
[d] 9.46 (OH).
[e] 9.38 (OH).
[f] 3.81 (OCH_3).
[g] 3.80 (OCH_3).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.91(3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.08 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.37–7.85 (9H, m, aromatic protons); 11.43 (1H, br. s,–CONH–); 13.01 (1H, br. s, –NHN=).

MS analysis *M* = 360. Positive-ion MS: *m*/*z* 361 $[M + H]^+$, 100%; *m*/*z* 315 $[M + H–C_2H_5OH]^+$, Negative-ion MS: *m*/*z* 359 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{20}H_{16}N_4O_3$): C (66.66%), H(4.84%), N(15.55%). Found: C (66.39%), H(4.70%), N(15.16%).

2.5. Ethyl 5-oxo-2-phenyl-4-[2-(4-nitrophenyl)hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (*1c*)

Preparative yield 90%; purified by recrystallization from ethanol, mp = 231–233 °C.

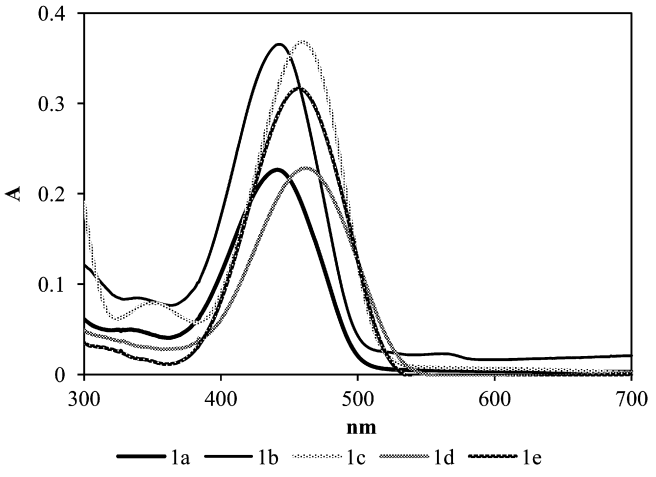


Fig. 1. Absorption spectra of **1a**–**1e** in NMP.

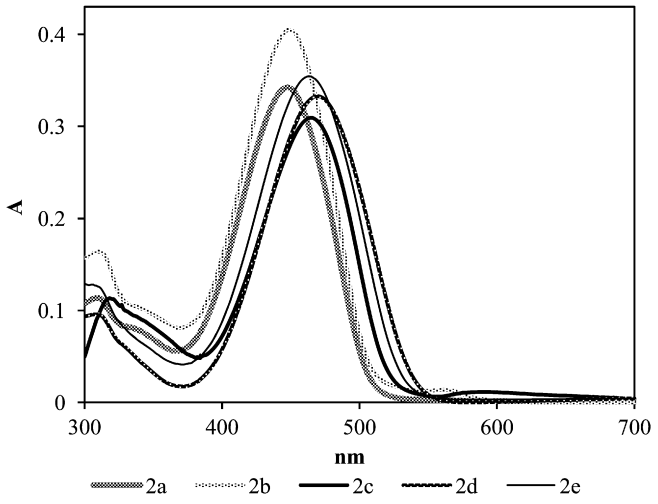


Fig. 2. Absorption spectra of **2a**–**2e** in NMP.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.24 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.20 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.39–8.30 (9H, m, aromatic protons); 11.52 (1H, br. s,–CONH–); 13.10 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.92 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.09 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.39–8.30 (9H, m, aromatic protons); 11.52 (1H, br.s,–CONH–); 13.31 (1H, br. s, –NHN=).

MS analysis *M* = 396. Positive-ion MS: *m/z* 397 $[M + H]^+$, 100%; *m/z* 355 $[M + H–C_2H_5OH]^+$, Negative-ion MS: *m/z* 395 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{19}H_{16}N_4O_5$): C(60%), H(4.24%), N(14.73%). Found: C (60.19%), H(4.33%), N(14.78%).

2.6. Ethyl 5-oxo-2-phenyl-4-[2-(4-hydroxyphenyl)hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (**1d**)

Preparative yield 57%; purified by recrystalization from ethanol, mp = 237–239 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.23 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.19 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 6.80–7.63 (9H, m, aromatic protons); 10.80 (1H, s, OH); 11.32 (1H, br. s, –CONH–); 13.18 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.89 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.06 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 6.80–7.63 (9H, m, aromatic protons); 10.80 (1H, s, OH); 11.20 (1H, br. s, –CONH–); 12.97 (1H, br. s, –NHN=).

Table 3
Absorption maxima (λ_{max}) and molar absorptivities (ε_{max}) in NMP at room temperature.

Dye	λ_{max} [nm] *E*, *Z* mixture	ε_{max} [L mol^{-1} cm^{-1}] *E*, *Z* mixture
1a	441	22700
1b	443	36500
1c	460	30800
1d	463	22800
1e	457	30100
2a	448	34200
2b	449	40000
2c	465	34000
2d	470	31300
2e	463	35400

Table 4
Solvent effect on absorption maxima of compounds **1a**, **1c** and **1e**.

Solvent	Dielectric constant	λ_{max} [nm]		
		1a	**1c**	**1e**
Dioxan	2.21	433	461	455
Acetone	20.7	434	460	449
NMP	32.0	441	471	457
Acetonitrile	37.5	434	461	450
DMSO	47.0	442	472	457

MS analysis *M* = 335. Positive-ion MS: *m/z* 351 $[M + H]^+$, 100%; *m/z* 306 $[M + H–C_2H_5OH]^+$, Negative-ion MS: *m/z* 350 $[M - H]^-$,100%; *m/z* 288$[M - H–C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{19}H_{17}N_3O_4$): C (64.95%), H(4.88%), N(11.96%). Found: C (64.81%), H(4.92%), N(11.75%).

2.7. Ethyl 5-oxo-2-phenyl-4-[2-(4-methoxyphenyl)hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (**1e**)

Preparative yield 82%; purified by recrystallization from ethanol, mp = 177–179 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.24 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 3.80 (3H, s, OCH_3); 4.20 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.01–7.65 (9H, m, aromatic protons); 11.35 (1H, br. s, –CONH–); 13.14 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.91 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 3.79 (3H, s, OCH_3); 4.08(2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.01–7.65 (9H, m, aromatic protons); 11.24 (1H, br. s, –CONH–); 13.00 (1H, br. s, –NHN=).

MS analysis *M* = 335. Positive-ion MS: *m/z* 351 $[M + H]^+$, 100%; *m/z* 306 $[M + H–C_2H_5OH]^+$, Negative-ion MS: *m/z* 350 $[M - H]^-$,100%; *m/z* 288$[M - H–C_2H_5OH]^-$.

Elemental analysis: calculated ($C_{20}H_{19}N_3O_4$): C (65.74%), H(5.24%), N(11.5%). Found: C (65.81%), H(5.62%), N(11.65%).

2.8. Ethyl 5-oxo-2-(naphthalen-2-yl)-4-(2-phenylhydrazonyl)-4,5-dihydro-1H-pyrrole-3-carboxylate(**2a**)

Preparative yield 87%; purified by recrystallization from ethyl-acetate, mp = 338–340 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.21 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.22 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.09–8.22 (12H, m, aromatic protons); 11.53 (1H, br. s, –CONH–); 13.15 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.82 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.09 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.09–8.22 (12H, m, aromatic protons); 11.42 (1H, br. s,–CONH–); 13.06 (1H, br. s, –NHN=).

MS analysis *M* = 385. Positive-ion MS: *m/z* 386 $[M + H]^+$, *m/z* 340 $[M + H–C_2H_5OH]^+$,100%, Negative-ion MS: *m/z* 384 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{23}H_{19}N_3O_3$): C (71.67%), H(4.97%), N(10.90%). Found: C (71.50%), H(5.01%), N(10.88%).

2.9. Ethyl 5-oxo-2-(naphthalen-2-yl)-4-[2-(4-cyanophenyl) hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (**2b**)

Preparative yield 69%; purified by reprecipitation from dioxan, cyclohexane, mp = 273–275 °C. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.20 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.21 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2); 7.39–8.26 (11H, m, aromatic protons); 11.63 (1H, br. s,–CONH–); 13.05 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.82 (3H, t, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_3); 4.09 (2H, q, 3H, t, ^3J = 7.1 ± 0.2 Hz, CH_2);

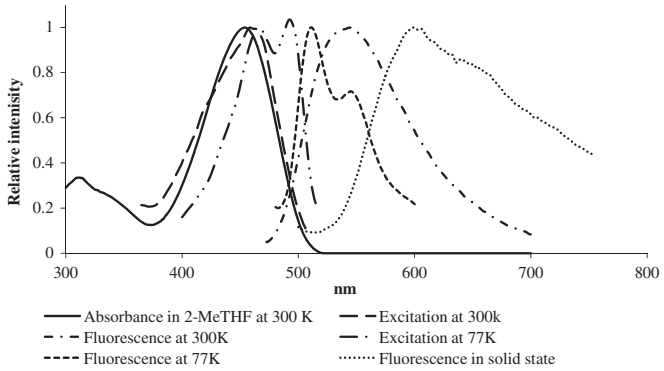


Fig. 3. Absorption at room temperature (MTHF) and excitation and emission spectra at low temperature (MTHF) of compound **1c** together with its solid-state emission at room temperature.

7.39–8.26 (11H, m, aromatic protons); 11.56 (1H, br. s, –CONH–); 13.20 (1H, br. s, –NHN=).

MS analysis $M = 410$. Positive-ion MS: m/z 411 $[M + H]^+$, m/z 365 $[M + H–C_2H_5OH]^+$,100%, Negative-ion MS: m/z 409 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{24}H_{18}N_4O_3$): C (70.23%), H(4.42%), N(13.65%). Found: C (69.99%), H(4.32%), N(13.60%).

2.10. Ethyl 5-oxo-2-(naphthalen-2-yl)-4-[2-(4-nitrophenyl) hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (**2c**)

Preparative yield 86%; purified by reprecipitation from dioxan, cyclohexane, mp = 272–275 °C. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.21 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.22 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.42–8.32 (11H, m, aromatic protons); 11.63 (1H, br. s, –CONH–); 13.16 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.84 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.10 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.42–8.32 (11H, m, aromatic protons); 11.63 (1H, br. s, –CONH–); 13.32 (1H, br. s, –NHN=).

MS analysis $M = 446$. Positive-ion MS: m/z 447 $[M + H]^+$, 100%; m/z 405 $[M + H–C_2H_5OH]^+$, Negative-ion MS: m/z 445 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{23}H_{18}N_4O_5$): C(64.18%), H(4.22%), N(13.02%). Found: C (64.39%), H(4.33%), N(13.08%).

2.11. Ethyl 5-oxo-2-(naphthalen-2-yl)-4-[2-(4-hydroxyphenyl) hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (**2d**)

Preparative yield 80%; purified by reprecipitation from dioxan, cyclohexane, mp = 256–258 °C. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.21 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.21 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2), 6.84–8.22 (11H, m, aromatic protons); 9.46 (1H, s, OH); 11.45 (1H, br. s, –CONH–); 13.26 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.82 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 4.07 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 6.84–8.22 (11H, m, aromatic protons); 9.48 (1H, s, OH); 11.32 (1H, br. s, –CONH–); 13.03 (1H, br. s, –NHN=).

MS analysis $M = 401$. Positive-ion MS: m/z 402 $[M + H]^+$, m/z 356 $[M + H–C_2H_5OH]^+$,100%, Negative-ion MS: m/z 400 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{23}H_{19}N_3O_4$): C (68.82%), H(4.77%), N(10.47%). Found: C (68.99%), H(4.62%), N(10.50%).

2.12. Ethyl 5-oxo-2-(naphthalen-2-yl)-4-[2-(4-methoxyphenyl) hydrazono]-4,5-dihydro-1H-pyrrole-3-carboxylate (**2e**)

Preparative yield 71%; purified by reprecipitation from dioxin, cyclohexane, mp = 230–232 °C. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *Z* isomer: 1.22 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 3.81 (3H, s, OCH_3); 4.21 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.00–8.22 (11H, m, aromatic protons); 11.47 (1H, br. s, –CONH–); 13.22 (1H, br. s, –NHN=).

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm) *E* isomer: 0.82 (3H, t, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_3); 3.80 (3 ± H, s, OCH_3); 4.08 (2H, q, 3H, t, $^3J = 7.1 \pm 0.2$ Hz, CH_2); 7.00–8.22 (11H, m, aromatic protons); 11.35 (1H, br. s,–CONH–); 13.04 (1H, br. s, –NHN=).

MS analysis $M = 415$. Positive-ion MS: m/z 416 $[M + H]^+$, m/z 370 $[M + H–C_2H_5OH]^+$,100%, Negative-ion MS: m/z 414 $[M - H]^-$, 100%.

Elemental analysis: calculated ($C_{24}H_{21}N_3O_4$): C (69.39 %), H(5.10 %), N(10.11 %). Found: C (69.17 %), H(4.95 %), N(10.90 %).

3. Results and discussions

3.1. Synthesis and structure of the dyes

Five dyes were synthesized from each pyrrolinone ester (Scheme 1, Table 1). Reaction yields were relatively high, always over 50%. The colorants synthesized from 2-naphthyl pyrrolinone ester **2** were less soluble than those derived from the phenyl analog in common solvents.

All compounds exist in DMSO-D_6 solution as a mixture of two components the content of which can change slightly during time. A complete NMR analysis was performed for ^{15}N-labeled compound **1a** in our previous study [19]. It was shown there, that it is possible to differentiate between *E* and *Z* isomers of the hydrazone tautomer, since especially ^{1}H chemical shifts (Table 2) of the ethoxy group protons can be used as a decisive indicator. Furthermore, the ^{1}H chemical shifts of the (CO) NH protons in *Z*- forms are

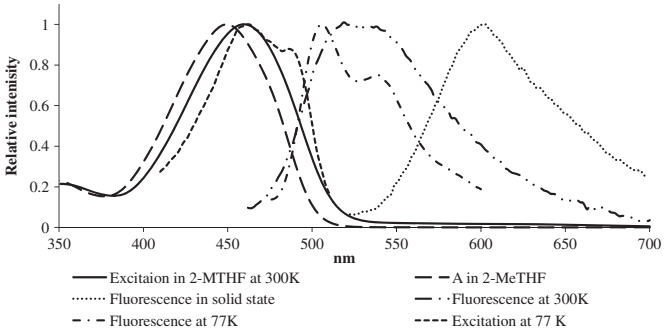


Fig. 4. Absorption at room temperature (MTHF) and excitation and emission spectra at low temperature (MTHF) of compound **2c** together with its solid-state emission at room temperature.

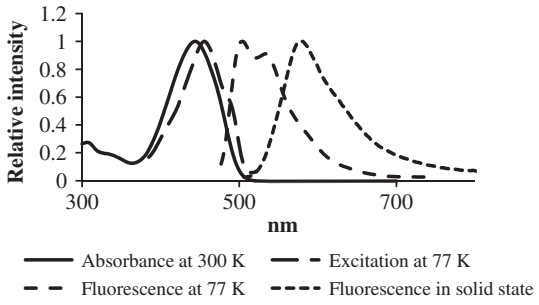


Fig. 5. Absorption at room temperature (MTHF) and excitation and emission spectra at low temperature (MTHF) of compound **2a** together with its solid-state emission at room temperature.

shifted to marginally higher field with respect to those in the *E* isomer in all cases. The % of *E* and *Z* was calculated by comparing the intensity of the peak related to aliphatic protons (ethoxy group). The fraction of *Z* isomer in a mixture is always higher. We mention the opposite conformation of 3-carbethoxy group in both isomers (*s-trans* for *Z*- and *s-cis* for *E* isomer), which was proved by NMR in our previous study [19].

3.2. Absorption

The absorption spectra of all ten derivatives were measured in NMP at room temperature. The spectra are shown on Figs. 1 and 2 and the spectral data are summarized in Table 3. The spectral shapes are broad without any vibronic structure. The trends are quite clear. There is a moderate bathochromic (5–8 nm) and hyperchromic (3500–8500 L mol^{-1} cm^{-1}) shift when going from the *2*-phenyl to the *2*-(2-naphthyl) derivatives. Both electron-donating and electron-withdrawing substituents in *para* position of phenyl-hydrazonyl moiety cause a significant bathochromic (19 nm for **1c**) and hyperchromic (13800 L mol^{-1} cm^{-1} for **1b**) shift with respect to parent compounds **1a** and **2a**.

The dyes are essentially insoluble in non-polar solvents and show slight positive solvatochromism in polar solvents (Table 4). The longest wavelength maxima were found in DMSO and NMP, although the latter shows a lower dielectric constant than acetonitrile. Thus probably some specific solute-solvent interaction (e.g. H-bonding) moderately affects the position of spectral maxima.

3.3. Fluorescence

Fluorescence spectroscopy was carried out in three different environments: in solution, in a frozen solvent glass (MTHF) and in the polycrystalline solid state. While the effect of the 2-aryl unit on the fluorescence spectra was only marginal, the substituent effect in the *para* position of phenyl-hydrazonyl unit was crucial and its variation caused dramatic changes in fluorescence. Generally, all ten compounds fluoresce in rigid environments (solid state and low temperature solvent glass), but only the cyano and nitro derivatives (**1b**, **2b** and **1c**, **2c**) show fluorescence in solution at room temperature. The ability to fluoresce in any environment is somewhat surprising for nitro substituted compounds absorbing at wavelengths lower than 500 nm (Figs. 3 and 4), because the $n\pi^*$ triplet state localized on nitro group is in such cases usually lower than the lowest $\pi\pi^*$ singlet state and intersystem crossing according to El-Sayed rule dominates [21].

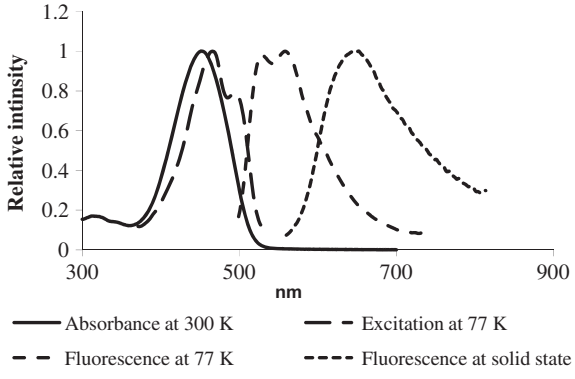


Fig. 6. Absorption at room temperature (MTHF) and excitation and emission spectra at low temperature (MTHF) of compound **1e** together with its solid-state emission at room temperature.

All compounds fluoresce in low temperature MTHF glass (e.g. compound **2a** and **1e** on Figs. 5 and 6). Low temperature fluorescence data for the 2-phenyl set are summarized in Table 5. A bathofluoric shift of low temperature fluorescence emission maxima of their *2*-(2-naphth-2-yl) analogs is only marginal (e.g. 3 nm when going from **1a** to **2a**). All compounds show resolved vibronic structure in their low temperature emission spectra with similar intensity of 0–0 and 0–1 vibronic sub-bands. The shape of fluorescence excitation spectra depends more on a character of substituent. In all cases the maximum corresponds to 0–1 vibronic transition. 0–0 vibronic sub-band is a local maximum for electron-donor substituted derivatives and is detectable only as a shoulder for neutral or electron-acceptor substituted derivatives.

Compounds **1b**, **2b**, **1c** and **2c** fluoresce in solution at room temperature with moderate intensity (Table 5). The spectra are rather blurred, and it suggests that the emission maxima correspond to 0–1 vibronic sub-band. The excitation maxima are shifted few nanometers to higher wavelength with respect to the absorption maxima in most cases, a feature which may indicate a dominant role of the fluorescence of the isomer absorbing at longer wavelengths (probably the more planar *Z* isomer according to DFT calculations for **1a** [19]). Such difference in fluorescence efficiency between *E* and *Z* isomers is not rare; it has recently been observed for arylmethyleneoxindoles [22]. Finally, the ability of the compounds with exocyclic double bond to fluoresce only in a rigid medium preventing the competitive *E*/*Z* isomerization process is quite general; noted for both arylmethylidene –oxindoles [22] and –pyrrolinones [13]. Furthermore, the positive effect of an electron-accepting substituent on the fluorescence efficiency in solution was observed not only for the above mentioned arylmethylidene –pyrrolinones [13,23], but also for arylmethylidene –oxazolones [20,23], –imidazolones and –butenolides [23]. The explanation probably comes from the study on hemithioindigo *E*/*Z* photoisomerization, in which the authors have shown, that electron-accepting substituent on stilbene half of the molecule decreases the reaction rate by several orders of magnitude with respect to a suitably placed electron-donor group [24]. Consequently, the higher φ_F (Table 5) of **1c** (**2c**) compared to **1b** (**2b**) may attributed to the stronger electron-accepting character of a nitro compared to a cyano group. Unfortunately, the exact evidence of *E*/*Z* photoisomerization of the compounds under study was not possible because of relatively fast back (dark) thermal isomerization.

Least all of the compounds fluoresce in the polycrystalline polycrystalline solid state (Figs. 3–6, Table 5). This phenomenon supports our suggestion that competitive photoisomerization must be hindered in a rigid environment. Unfortunately, as the X-ray structure of molecular aggregation in crystal is not available, the detailed discussion of the ability of solid-state fluorescence would be only speculative.

Table 5
Fluorescence excitation and emission maxima [nm] of 0–0 and 0–1 vibronic bands (MTHF at 77 K), solid-state fluorescence maxima at room temperature and fluorescence maxima and quantum yields at room temperature.

Compound	Excitation (MTHF, 77 K)		Emission (MTHF, 77 K)		Emission (Solid)	Emission (MTHF, 300 K)	
	0–1	0–0	0–0	0–1		λ_{max} [nm]	φ_F
1a (**2a**)	449	sh	501	534	554 (580)	–	–
1b (**2b**)	452	sh	492	524	565 (588)	527 (540)	0.05 (0.06)
1c (**2c**)	455	481	503	534	593 (599)	524 (545)	0.10 (0.18)
1d (**2d**)	470	493	542	574	669 (672)	–	–
1e (**2e**)	466	496	529	559	647 (609)	–	–

4. Conclusion

Continuing a systematic research of dyes derived from pyrrolinone esters, ten azo dyes were prepared by a diazotization of *para* substituted anilines and consequent azo coupling of these diazonium salts with two pyrrolinone esters as passive components. All dyes were confirmed as keto-hydrazone tautomers and were found as a mixtures of *E* and *Z* isomers with respect to the exocyclic C=N bond, in contrast to similar arylmethylidene −pyrrolinones, that arise from the condensation of aldehydes with pyrrolinones which exist exclusively as *Z* isomers with respect to exocyclic C=C bond [13]. The absorption spectra are quite similar irrespective of either substituent or solvent. Fluorescence on the other hand is strongly dependent on the character of the substituent. All compounds fluoresce in a low temperature solvent glass and in the solid state and only 4-cyano and 4-nitro derivatives show fluorescence in room temperature solution. An explanation based on a comparative *E*/*Z* isomerization and fluorescence after excitation, was proposed.

Acknowledgments

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References

[1] Zollinger H. Color chemistry. Weinheim: VCH; 1991.
[2] Herbst M, Hunger K. Industrial organic pigments. Weinheim: VCH; 1993.
[3] Ball P, Nicholls CH. Azo-hydrazone tautomerism of hydroxyazo compounds – a review. Dyes Pigm 1982;3:5–26.
[4] Gordon PF, Gregory P. Organic chemistry in colour. Berlin: Springer-Verlag; 1983.
[5] El Halabieh RH, Mermut O, Barrett CJ. Using light to control physical properties of polymers and surfaces with azobenzene chromophores. Pure Appl Chem 2004;76:1445–65.
[6] Schmidt MU, Brüning J, Wirth D, Bolte M. Two azo pigments based on β-naphtol. Acta Cryst 2005;C64:o474–7.
[7] Skoweranda J, Bukowska-Strzyzewska M, Strzyzewski W. Molecular structure of isopropyl 1-phenyl-4-phenylhydrazono-5-oxo-3-pyrazolecarboxylate. J Chem Cryst 1994;24:517–20.
[8] Griffiths J. Prediction of colour change in dye equilibria I – azo and hydrazone tautomers and anions of 4-phenylazo-1-naphthols. J Soc Dyers Colourists 1972;88:106–9.
[9] Mustroph H, Bartel R. Studies on UV/Vis absorption spectra of azo dyes. vi. the effect of substituents on the color derivatives of 1-phenylazo-2-naphtols. J Prakt Chem 1982;324:743–52.
[10] Nikolov P, Fratev F, Stoyanov S, Polansky OE. Fluorescence and absorption spectra of phenylazopyrazolone dyes. Z Naturforsch 1981;36a:191–6.
[11] Joshi H, Kamounah FS, Gooijer C, van der Zwan G, Antonov L. Excited state intramolecular proton transfer in some tautomeric azo dyes and Schiff bases containing an intramolecular hydrogen bond. J Photochem Photobiol A Chem 2002;152:183–91.
[12] Adam JM, Dalvi P, Ekkundi VS, Bacher JP, Tiwari S. WO patent 04/083170; 2004.
[13] Vyňuchal J, Luňák Jr S, Hatlapatková A, Hrdina R, Lyčka A, Havel L, et al. The synthesis, absorption, fluorescence and photoisomerisation of 2-aryl-4-arylmethylidene-pyrroline-5-ones. Dyes Pigm 2008;77:266–76.
[14] Morton CJH, Riggs RL, Smith DM, Westwood NJ, Lightfoot P, Slawin AMZ. Synthetic studies related to diketopyrrolopyrrole (DPP) pigments. Part 2: the use of esters in place of nitriles in standard DPP syntheses: Claisen-type acylations and furopyrrole intermediates. Tetrahedron 2005;61:727–38.
[15] Morton CJH, Gilmour R, Smith DM, Lightfoot P, Slawin AMZ, MacLean EJ. Synthetic studies related to diketopyrrolopyrrole (DPP) pigments. Part 1: the search for alkenyl DPPs. Unsaturated nitriles in standard DPP syntheses: a novel cyclopenta[c]pyrrolone chromophore. Tetrahedron 2002;58:5547–65.
[16] Luňák Jr S, Vyňuchal J, Vala M, Havel L, Hrdina R. The syntheses, absorption and fluorescence of polar diketo-pyrrolo-pyrroles. Dyes Pigm 2009;82:102–8.
[17] Luňák Jr S, Havel L, Vyňuchal J, Horáková P, Kučerík J, Weiter M, et al. The geometry and absorption of diketo-pyrrolo-pyrroles substituted with various aryls. Dyes Pigm 2010;85:27–36.
[18] Chamberlain T. WO patent 01/74950; 2001.
[19] Lyčka A, Luňák Jr S, Aysha T, Holuša R, Hrdina R. A ^{1}H, ^{13}C and ^{15}N NMR spectroscopic and GIAO DFT study of ethyl 5-oxo-2-phenyl-4-(2-phenylhydrazono)-4,5-dihydro-1H-pyrrole-3-carboxylate. Tetrahedron Lett 2010;51:3149–51.
[20] Bondarev S, Knyukshto V, Stepuro V, Stupak A, Turban A. Fluorescence and electronic structure of the laser dye DCM in solutions and in polymethylmethacrylate. J Appl Spectrosc 2004;71:194–201.
[21] Krasovitskii BM, Bolotin BM. Organic luminescent materials. Weinheim: VCH; 1988.
[22] Luňák Jr S, Horáková P, Lyčka A. Absorption and fluorescence of arylmethylidenoxindoles and isoindigo. Dyes Pigm 2010;85:171–6.
[23] Bourotte M, Schmitt M, Follenius-Wund A, Pigault C, Haiech J, Bourguignon JJ. Fluorophores related to the green fluorescent protein. Tetrahedron Lett 2004;45:6343–8.
[24] Cordes T, Schadendorf T, Priewisch B, Rück-Braun B, Zinth W. The Hammett relationship and reactions in the excited electronic state: hemithioindigo *Z*/*E*-photoisomerization. J Phys Chem A 2008;112:581–8.