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The synthesis, absorption, fluorescence and photoisomerisation of 2-aryl-4-arylmethylidene-pyrroline-5-ones

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Abstract

Base catalyzed Claisen–Schmidt type condensation of ethyl-4,5-dihydro-5-oxo-2-phenyl(1*H*)pyrrole-3-carboxylate and its 2-biphenylyl analogue with various aldehydes was studied. The absorption and fluorescence spectra of ethyl-4,5-dihydro-5-oxo-2-aryl-4-(arylmethylidene)-(1*H*)pyrrole-3-carboxylate at both room (300 K) and low (77 K) temperatures were analyzed. *E*–*Z* photoisomerisation was observed for all derivatives; the *Z*-isomer was confirmed as being thermodynamically stable by NMR spectroscopy. PM3 quantum chemical method was used for ground state geometry calculations of the *Z*-isomers, while INDO/S calculations enabled interpretation of the absorption spectral shifts. Photoisomerisation forms the main deactivation channel after excitation in fluid solution, in contrast to rigid frozen glass, where fluorescence is preferred.

Keywords: 2-Aryl-4-arylmethylidene-pyrroline-5-ones; Photoisomerisation; Fluorescence; Pyrrolinone ester

1. Introduction

Ethyl-4,5-dihydro-5-oxo-2-phenyl(1*H*)pyrrole-3-carboxylate (pyrrolinone ester, **I**) has become an interesting intermediate in the colorant chemistry in recent years. The ester is the first step reaction product in the syntheses of diketo-pyrrolopyrrole (DPP) pigments from aromatic nitriles and the diester of succinic acid under basic conditions of *tert*-amylalcohol and *tert*-amylalcoholate [1]. However, it cannot be isolated due to its reactivity in alkaline solution with the aromatic nitrile molecule. If a special base is used, such as lithium-diisopropylamine, compound **I** can be isolated at low temperature [2]. An easier synthesis of **I** is based on the reaction of ethylbenzoylacetate and methylchloroacetate as described below.

The keto and ester groups of pyrrolinone ester **I** activate the carbon atom of the methylene group in position 4 of the pyrrolinone ring, allowing the reaction of **I** with aldehydes and diazonium salts. The products of the coupling of **I** with various diazotized aromatic amines have been described [3] and those of the Claisen–Schmidt type condensation of **I** with aldehydes have been described as potential colorants [4,5]. The pyrrolinone ester is able to create a wide range of asymmetric DPP compounds, which can be used in the different applications [6–12]. Morton et al. [13,14] described the reaction of pyrrolinone ester with esters and chlorides of aromatic acids; the oxidation [15] of pyrrolinone ester to bipyrrolinonylidene ester should be mentioned. All of these published reactions of the compound **I** are summarized in Fig. 1. We have synthesized five simple arylmethylidene-pyrrolinones (**Ia**–**Ie**) by the

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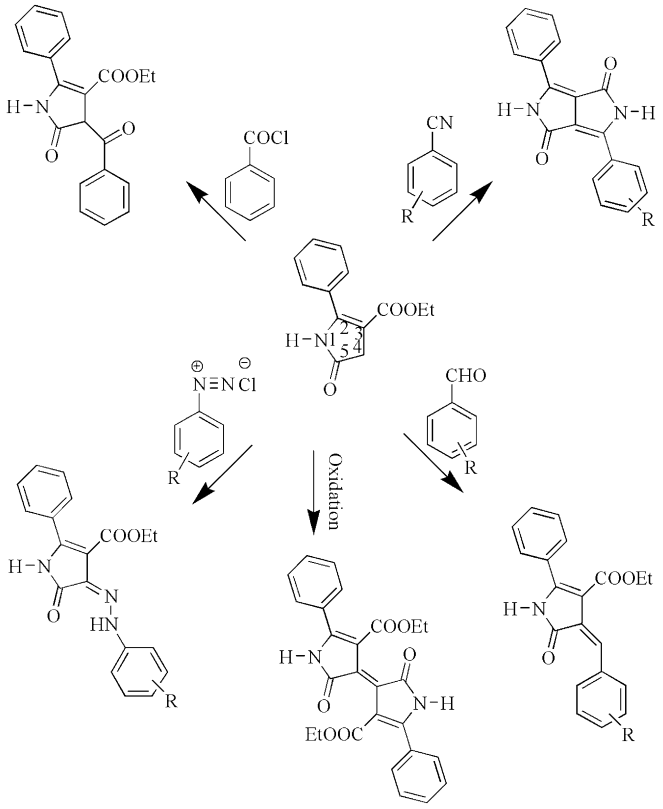


Fig. 1. Reactions of the compound **I**.

condensation of **I** with various aromatic aldehydes in order to study their geometry, electronic spectral properties and excited state behaviour. Furthermore, the 2-biphenylyl analogue (**II**) was synthesized as a key intermediate for the synthesis of a further five-related compounds (**IIa**–**IIe**) each with an extended π-conjugated system.

2. Results

2.1. Synthesis

The intermediate **I** was prepared from ethylbenzoylacetate and methylchloroacetate. Intermediate **II** was prepared in a similar way (ethylbromoacetate was used), but as its starting material ethyl-4-biphenyloylacetate was not commercially available, it was prepared by Claisen condensation according to Fig. 2. The reactions of **I** and **II** with aldehydes were carried out in toluene in the catalytic presence of piperidine according to the general scheme shown in Fig. 3. Ten derivatives **Ia**–**Ie** and **IIa**–**IIe** were prepared (Table 1).

2.2. UV/vis absorption spectra

The absorption spectra of **Ia**–**Ie**, and **IIa**–**IIe** at room temperature were measured in dimethylsufoxide (DMSO) and 2-methyl-tetrahydrofuran (2-Me-THF). The spectra were structureless and can be characterized by the position of the absorption maximum and the molar absorptivity (Table 2).

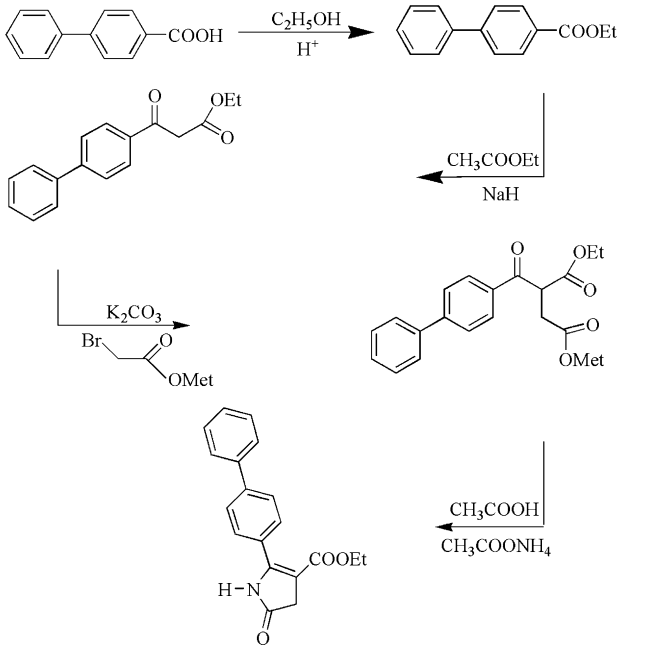


Fig. 2. Synthesis of the compound **II**.

The spectra in DMSO are shown in Fig. 4 and in 2-Me-THF in Figs. 5–9, together with fluorescence spectra. Molar absorptivities were estimated only in DMSO, because of inadequate solubility in 2-Me-THF.

2.3. Fluorescence excitation and emission spectra

Fluorescence emission and excitation spectra were measured in 2-Me-THF forming a transparent glass at 77 K. **Ie** and **IIe** were the only compounds for which weak room temperature fluorescence was observed with no significant difference between the absorption and fluorescence excitation (Fig. 5). In contrast, all 10 compounds fluoresced intensely at 77 K (Figs. 6–9). Vibronic progressions can be observed in both the excitation and emission spectra, being best resolved for **Id** and **IId** (Fig. 6), partially resolved for **Ia**, **Ib** (Fig. 7), **IIa**, **IIb** (Fig. 8), **Ie** and **IIe**, and unresolved for **Ic** and **IIc** (Fig. 9). Fluorescence emission maximum corresponded to 0–1 vibronic transition in all cases, while excitation maximum mostly to 0–2 vibronic transition in 2-phenyl (e.g. Fig. 7) and 0–1 in 2-biphenyl (e.g. Fig. 8) series.

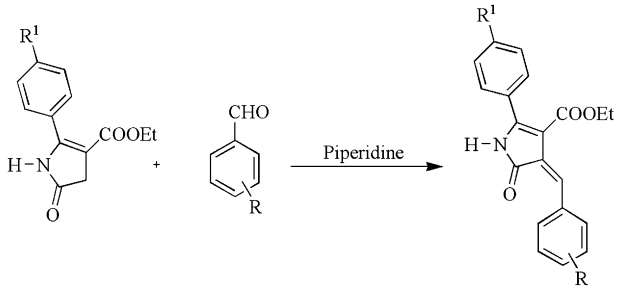
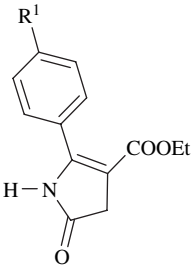
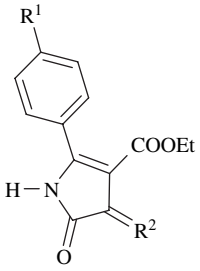
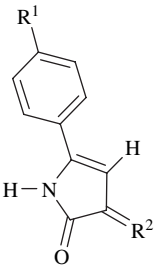
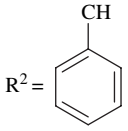
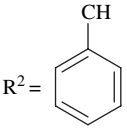
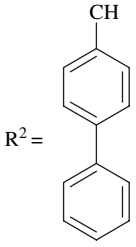
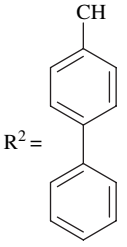
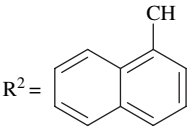
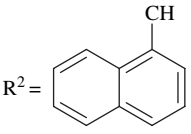
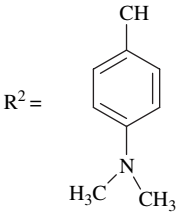
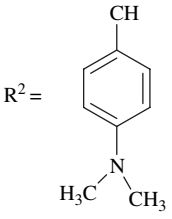
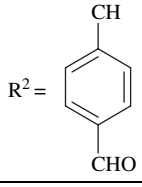
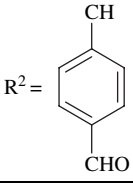


Fig. 3. General scheme of a reaction of the compound **I** ($R^1 = H$) or **II** ($R^1 = Ph$) with aldehyde.

Table 1
Synthesized intermediates (**I**, **II**) and derivatives (**Ia**–**Ie**, **IIa**–**IIe**) and model compounds for quantum chemical calculations (**Ia^m**–**Ie^m**, **IIa^m**–**IIe^m**)

			
	Ia (R^1 = H) **IIa** (R^1 = Ph)		**Ia^m** (R^1 = H) **IIa^m** (R^1 = Ph)	
	Ib (R^1 = H) **IIb** (R^1 = Ph)		**Ib^m** (R^1 = H) **IIb^m** (R^1 = Ph)	
I (R^1 = H) **II** (R^1 = Ph)	**Ic** (R^1 = H) **IIc** (R^1 = Ph)		**Ic^m** (R^1 = H) **IIc^m** (R^1 = Ph)	
	Id (R^1 = H) **IId** (R^1 = Ph)		**Id^m** (R^1 = H) **IId^m** (R^1 = Ph)	
	Ie (R^1 = H) **IIe** (R^1 = Ph)		**Ie^m** (R^1 = H) **IIe^m** (R^1 = Ph)	

2.4. Photoisomerisation

2.4.1. HPLC and MS evidence

Acetonitrile solutions of all compounds are sensitive to daylight. HPLC of **Ie** may serve as an example (Fig. 10). The chromatogram of a sample prepared in the dark showed one peak, confirming the purity of the compound. When this sample (in a Pyrex tube) was left in daylight for 1 h, the intensity of the original peak decreased and a second peak appeared at a shorter elution time. After some time from the start of irradiation the ratio of the intensity of the peaks did not change, as the photostationary state was achieved. Both samples (irradiated and dark) did not show any changes, when left in the dark for one day or when heated to reflux in acetonitrile. The

Table 2
Absorption and fluorescence maxima in 2-Me-THF, absorption maxima and molar absorptivities, ε, in DMSO

Compound no.	2-Me-THF		DMSO		
	Absorption maximum (300 K) [nm]	Fluorescence maximum (300 K) [nm]	Fluorescence maximum (77 K) [nm]	Absorption maximum (300 K) [nm]	ε [l cm^{-1} mol^{-1}]
Ia	403	–	522	412	11 900
IIa	408	–	532	417	14 900
Ib	415	–	538	425	16 500
IIb	425	–	509, 542	434	21 000
Ic	413	–	555	419	12 300
IIc	421	–	570	427	16 600
Id	451	–	530, 564	471	37 100
IId	462	–	537, 571	478	37 300
Ie	422	570	550	433	12 300
IIe	433	577	522, 556	441	15 100

2-Me-THF is related to the absorption maximum (300 K), resp. fluorescence maximum (300 K,77 K); DMSO is only related to the absorption maximum (300 K) and molar absorptivities.

mass spectra of the irradiated and dark samples were identical, including the same molecular peak. The absorption spectra of all nine photoproducts (**IIb** was not sufficiently soluble), which were measured by diode-array detector showed similar hypsochromic shifts (Fig. 11 for **Ie**) from 8 nm to 12 nm. With respect to absorption intensity, all nine photoproducts showed hypochromic shift compared to the original isomer.

2.4.2. NMR

There were two sets of signals in both ^{1}H and ^{13}C NMR spectra of compounds **Ib** and **Ic**, one very strong immediately after dissolution of compounds **Ib** and **Ic** in hexadeuteriodimethyl sulfoxide; the proportion of the minor compound increased during standing in solution. The ratios of major:minor components were 1:0.5 (**Ib**) and 1:0.7 (**Ic**) after two weeks storage. The existence of *E*–*Z* isomerism in compounds **Ib** and **Ic** was anticipated. As NMR spectroscopy is capable of differentiating these two isomers, a method proposed by Cho et al. [16], based on the stereochemical dependence of ^{3}J (^{13}C, ^{1}H) coupling constants on a C=C double bond, was employed; herein Cho et al. [16] found that coupling constant of the carbon *trans* to the olefinic proton is considerably higher than that of carbon *cis* to the same proton using single crystal X-ray data in the solid state and heteronuclear Overhauser effect in solution. For our compounds, the stereochemical dependence of ^{3}J (^{13}C, ^{1}H) coupling constants was studied in the fragment HN–*C*(=O)–C(=C*H*–)–*C*(COOC$_2$H$_5$) having measured the proton-coupled ^{13}C NMR spectra of compounds **Ib** and **Ic** at a resolution >0.5 Hz/point. The results obtained are shown in Fig. 12. The NH–*C*=O resonances were in the range 166.7–168.7 ppm and *C*(COOC$_2$H$_5$) at 103.1–104.5 ppm, respectively, as proven using two-dimensional ^{1}H–^{13}C HMBC. *Z*-isomers were present immediately after dissolution of compounds **Ib** and **Ic** in hexadeuteriodimethyl sulfoxide, while mixtures of the *Z*- and *E*-isomers existed after some time of standing. Only the *Z*-isomers were described by Metten et al. [17] for the disubstituted (4-OCH$_3$ and 4′-COOH; 4-OCH$_3$ and 4′-H) analogues of **Ia**. The same behaviour was observed

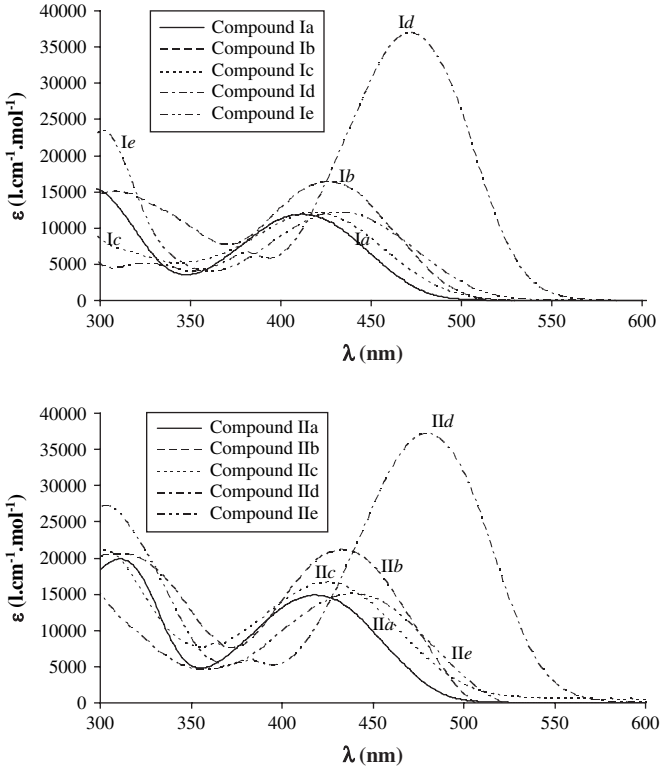


Fig. 4. Absorption spectra in DMSO.

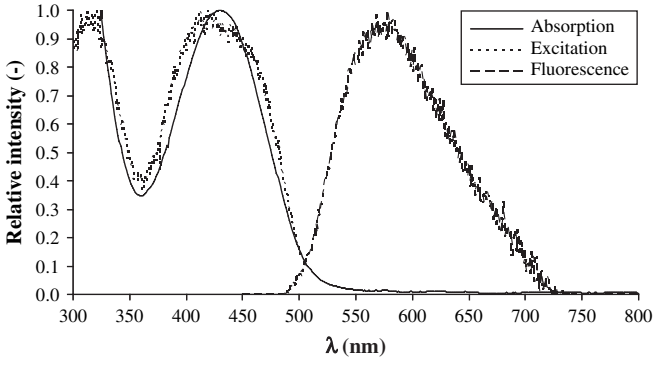


Fig. 5. Spectra of the compound **IIe** in 2-Me-THF at 300 K.

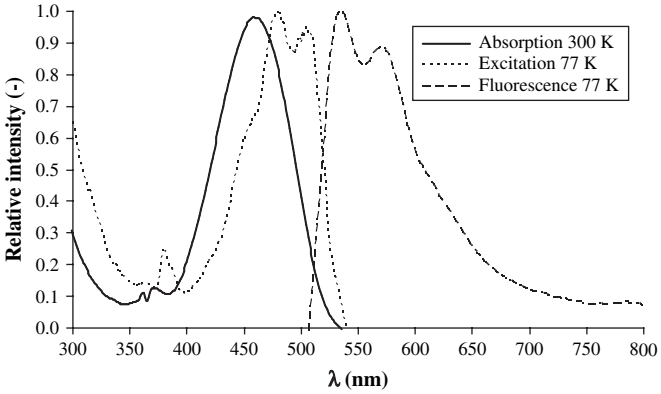


Fig. 6. Spectra of the compound **IId** in 2-Me-THF at 300 K and 77 K.

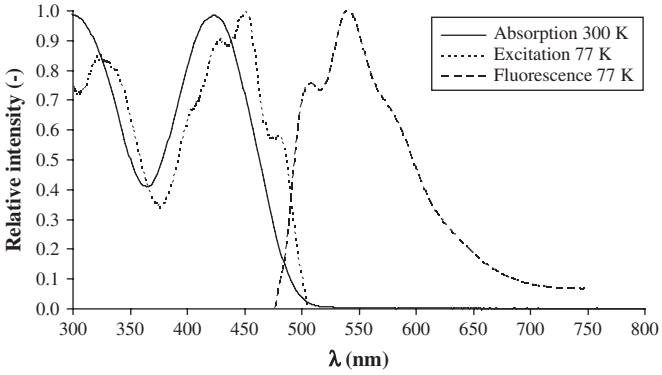


Fig. 8. Spectra of the compound **IIb** in 2-Me-THF at 300 K and 77 K.

for series **II**; compound **IIb** was excluded from this experiment due to its dissolubility.

2.5. Quantum chemical calculations

The WinMopac quantum chemical package was used and calculations were performed for 10 synthesized compounds (**Ia**–**Ie**, **IIa**–**IIe**) and 10 model compounds (**Ia^{m}**–**Ie^{m}**, **IIa^{m}**–**IIe^{m}**) in order to evaluate the effect of the 3-ethylester chain on both geometry and spectral properties.

The ground state geometry of the *Z*-isomers was calculated using PM3 Hamiltonian.

The models (**Ia^{m}**–**Ie^{m}**, **IIa^{m}**–**IIe^{m}**) are planar; the introduction of the ethylester chain at the 3-position of the pyrrolinone ring perturbs the planarity in the following manner: dihedral angle $\alpha = 37–38°$, $\beta < 2°$ and $\gamma = 61–64°$ for all compounds, except **Ic** and **IIc**, for which $\beta = 7–8°$ (see Fig. 13 for a notation). The sterically less hindered rotamer of **Ic** and **IIc** was taken into account.

INDO/S calculations of the excitation energies were carried out for the calculated geometries. The excitation energies of the lowest excited states of ππ* type were recomputed to the wavelengths of the spectral electronic transitions and are summarized in Table 3 together with the oscillator strengths and purity of the HOMO–LUMO character of the calculated S1 state. All monoexcited configurations were introduced to the configurational interaction (CI) and the contribution of the HOMO–LUMO configuration to the S0–S1 transition was >80% in all cases.

3. Discussion

The experimental evidence obtained by NMR spectroscopy for compounds **Ib**, **Ic**, **IIa**, **IIc**, **IId** and **IIe** shows that the structure of these compounds in non-irradiated solution corresponds to the *Z*-isomer. PM3 calculations predict the planarity of the 4-arylmethylidene-pyrrolinone component and high out-of-plane rotation of the 2-aryl-pyrrolinone moiety was imparted by the steric effect of the 3-ethylester chain for all of the *Z*-isomers, except for the naphthyl derivatives **Ic** and **IIc**, for which some non-planarity of the naphthyl-methylidene component was observed.

If **Ia^{m}** is considered as a basic chromophore, we can discuss the effect of three structural modifications on the absorption spectra namely, the influences of the 3-ethylester chain (only on the basis of the theoretical calculations), of enlargement of the π-conjugated system and of polar substituents in the *para*-position of the benzilidene ring. In general, these effects were clear and expected: the ethyl ester substituent caused a hypsochromic shift, as it is decreasing the planarity of the π-system, enlargement of the π-system and polar substitution produce a bathochromic shift. However, there are some

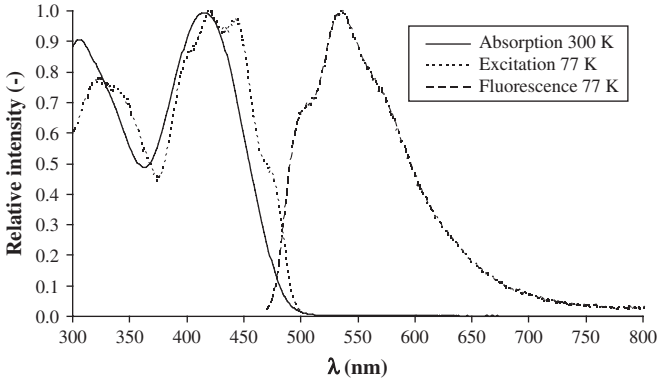


Fig. 7. Spectra of the compound **Ib** in 2-Me-THF at 300 K and 77 K.

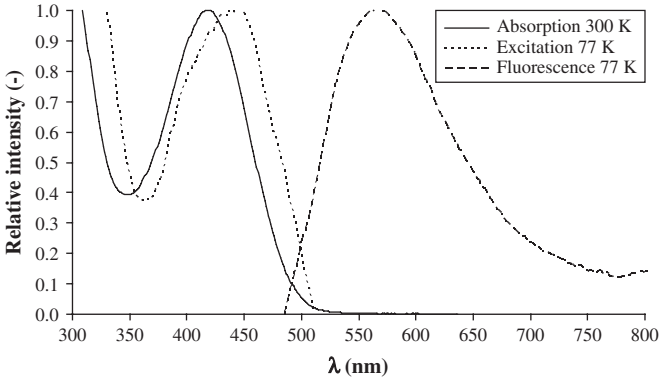


Fig. 9. Spectra of the compound **IIc** in 2-Me-THF at 300 K and 77 K.

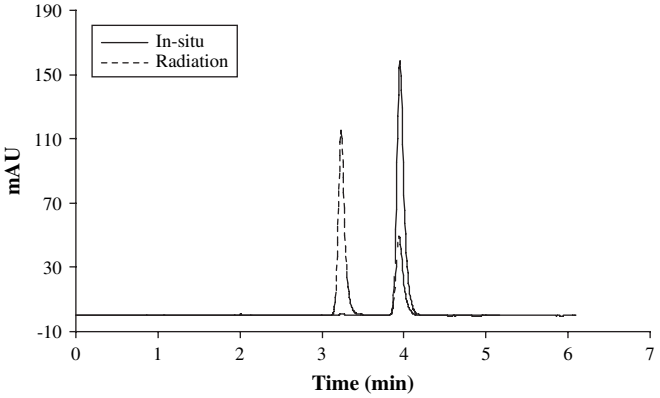


Fig. 10. Chromatogram of the compound **Ie** in situ and after radiation.

additional effects, which should be discussed in detail. Theory predicts that the effect of enlargement of a conjugated π-system is slightly greater in the case of the 4-position than the 2-position of the pyrrolinone ring. For the 2-biphenylyl analogues, bathochromic shifts of 10 nm (**Ia**^{m} → **IIa**^{m}) or 9 nm (**Ib**^{m} → **IIb**^{m}) were obtained, while for the 4-biphenylyl analogues 17 nm (**Ia**^{m} → **Ib**^{m}) or 16 nm (**IIa**^{m} → **IIb**^{m}) compared to parent phenyl were achieved. When the 3-ethylester chain is introduced, the difference is even higher, as the 2-aryl substituent is rotated out-of-plane (e.g. 18 nm (**Ia** → **Ib**) vs. 7 nm (**Ia** → **IIa**)). The hypsochromic shift imparted by 3-ethylester substitution was slightly lower in the phenyl (8 nm for **Ia**^{m} → **Ia**, 7 nm for **Ib**^{m} → **Ib**) than the biphenyl series (11 nm for **IIa**^{m}→ **IIa** and for **IIb**^{m} → **IIb**), because in the latter case, a relatively larger part of the π-system is rotated. The shifts in the experimental absorption maxima (2-Me-THF) support these theoretical results.

In an ideal case one should be able to correlate the computed λ_{00} with the spectral position of 0–0 vibronic progression of the absorption spectrum measured in a non-polar solvent. Unfortunately, as most of the studied compounds were insoluble in such solvents, data obtained in 2-Me-THF (which is less polar than DMSO) could only be used. Furthermore, 0–0 vibroni c transition was not progressed for some compounds, and so λ_{00} will be compared with the absorption maxima at 300 K. Such correlation is excellent only for **Ia**, **Ib**, **IIa** and **IIb** (difference less than 4 nm). For the naphthyl derivatives

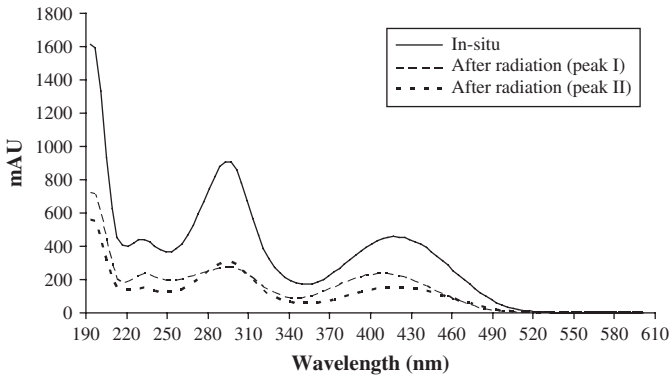


Fig. 11. Peak spectra of compound **Ie** from diode-array detector of HPLC equipment.

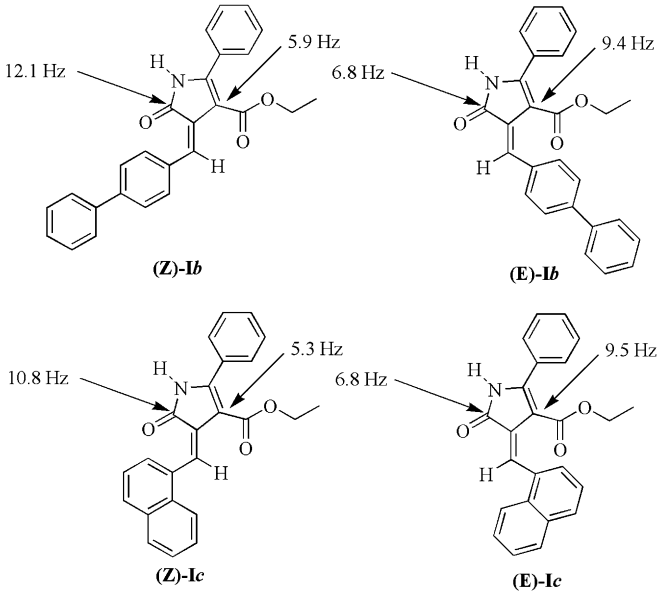


Fig. 12. Selected ^{3}J (^{13}C, ^{1}H) coupling constants of methylidene proton in compounds **Ib** and **Ic**.

Ic and **IIc**, the computed λ_{00} were higher than the experimental maxima (approximately 10 nm). In contrast, the experimental maxima for the polar derivatives **Ie**, **IIe** and especially **Id**, **IId** were at significantly longer wavelengths.

The absorption spectra in DMSO were bathochromically shifted with respect to 2-Me-THF, confirming the expected positive solvatochromism. This shift is the largest for **Id** and **IId** as these were the most polar compounds of all the derivatives.

Low temperature fluorescence emission and excitation spectra showed better resolved vibronic structure when going from a fluid to a rigid environment. Both the excitation and emission spectra of **Ic** and **IIc** were the least resolved (Fig. 9), indicating the higher degree of non-planarity. Such non-planarity was qualitatively predicted by PM3 (β angle of *Z*-isomer of **Ic** and **IIc** are about 7° on the contrary to <2° for all other derivatives). In our opinion the real deviation of planarity of **Ic** and **IIc** must be higher than computed, in order to explain the differences in resolution of vibronic sub-bands and shorter wavelengths of experimental absorption maxima with respect to computed λ_{00}.

The spectra obtained during HPLC measurements (e.g. Fig. 11) show that *E*-isomers are slightly hypsochromically shifted with respect to *Z*-isomers at room temperature (approximately 10 nm), that is usual for less thermodynamically stable isomers.

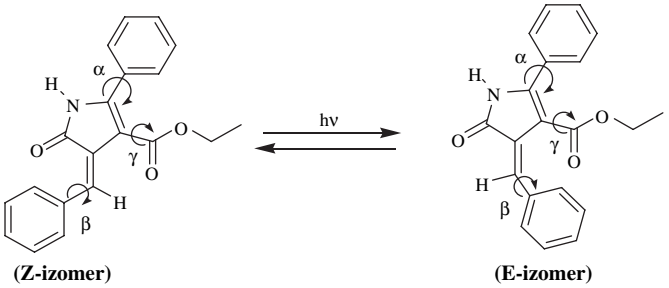


Fig. 13. Dihedral angle for *Z*- and *E*-isomers.

Table 3
INDO/S calculations of the position and intensity of the longest wavelength ππ* transition

Compound	λ_{00} [nm]	f_{osc}	HOMO–LUMO [%]	Model compound	λ_{00} [nm]	f_{osc}	HOMO–LUMO [%]
Ia	399	0.701	93	**Ia^{m}**	407	0.760	93
IIa	406	0.926	87	**IIa^{m}**	417	1.022	89
Ib	417	1.004	89	**Ib^{m}**	424	1.060	90
IIb	422	1.231	87	**IIb^{m}**	433	1.317	88
Ic	424	0.807	91	**Ic^{m}**	431	0.869	92
IIc	430	1.002	88	**IIc^{m}**	439	1.096	89
Id	415	0.860	92	**Id^{m}**	428	0.970	91
IId	421	1.076	89	**IId^{m}**	436	1.216	88
Ie	408	0.766	90	**Ie^{m}**	418	0.839	90
IIe	416	0.995	82	**IIe^{m}**	428	1.086	85

λ_{00} [nm] – wavelength of 0–0 vibronic transition of the longest wavelength ππ* transition, f_{osc} – oscillator strength, HOMO–LUMO [%] – participation of HOMO–LUMO configuration in CI.

We consider, that the rotation around the exocyclic double bond (in the ground state S0), that bond order is decreased in the lowest excited S1 (ππ*), is the main deactivation process after the excitation. This rotation occurs on S1 (ππ*) hypersurface starting from a geometry of *Z*-isomer (angle of rotation 180°), rotating to 90° and then either continuing to new *E*-isomer (angle of rotation 0°), or returning back to *Z*-isomer. If such rotation is disabled, e.g. by sterical hindrance of frozen environment in our case of 2-Me-THF at 77 K, then fluorescence becomes the dominating S1 → S0 deactivation process. Back thermal *E*–*Z* isomerisation was not observed, because of high energy barrier in S0 state. No evidence was found for triplet manifold to take part in the deactivation pathway.

We are unable to explain, why the formyl substituted derivatives **Ie** and **IIe** are the only ones showing weak room temperature fluorescence. We only mention that π-isoelectronic 2-phenyl-4-benzylidene-oxazol-5-ones show a similar behaviour, when substituted with various strong electron-acceptor groups in the *para*-position of benzylidene ring [18].

4. Experimental

4.1. Instrumental equipment

4.1.1. Absorption spectra

Perkin Elmer Lambda 35 was used for measuring absorption spectra.

4.1.2. Fluorescence spectra

Perkin Elmer LS 35 was used for measuring fluorescence spectra at room and low temperatures. 2-Methyl-tetrahydrofurane was used as a solvent to create organic frozen glass to measure low temperature fluorescence spectra.

4.1.3. High performance liquid chromatography

An HP 1090 M liquid chromatograph equipped with a UV diode-array detector, an automatic sample injector, a 3DR solvent delivery system, a thermostated column compartment and a Series 7994 A workstation (Hewlett-Packard, Palo Alto, CA USA) was used for all measurements. The flow rate of the mobile phase was kept at 1 ml min^{-1} and the temperature at 40 °C. The detection wavelength was set at 410 nm, resp. 510 nm (absorption maximum).

Acetonitrile (LiChrosolv gradient grade, Merck, Darmstadt, Germany) was used as obtained. Water was double distilled. Mobile phase was prepared by mixing in appropriate volume ratios directly in the HP 1090 M instrument from the components continuously stripped by a stream of helium. The samples were dissolved in pure acetonitrile to provide adequate response of the UV detector. Ten microlitres sample volumes were injected in each experiment.

4.1.4. Mass spectrometry

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.

4.1.5. Elemental analysis

EA 1108 FISONS instrument was used for elemental analysis.

4.1.6. Nuclear magnetic resonance

Bruker AVANCE 500 and AMX 360 NMR spectrometers, operating at 500.13 or 360.13 MHz for ^{1}H and 125.76 or 90.56 MHz for ^{13}C were used for measurements of ^{1}H and ^{13}C NMR spectra. The compounds were dissolved in hexadeuteriodimethyl sulfoxide. The ^{1}H and ^{13}C chemical shifts were referred to the central signal of the solvent ($\delta = 2.55$ (^{1}H) and 39.60 (^{13}C)). Positive values of chemical shifts denote shifts to higher frequencies.

4.2. Syntheses and analytics

4.2.1. Ethyl-4,5-dihydro-5-oxo-2-phenyl(1H) pyrrole-3-carboxylate (*I*)

Ethylbenzoylacetate (Aldrich 98%, 188.4 g, 0.980 mol) and methylchloroacetate (106.4 g, 0.985 mol) with sodium carbonate (142 g), 200 ml acetone, 233.4 ml ethyleneglycol dimethylether were added to the three-necked flask (volume 2 l) with thermometer and refluxing condenser and stripped by stream of nitrogen. The reaction mixture was refluxed for 24 h. Acetone was continuously added into the reaction mixture to keep the constant volume due to evaporating off. Methylchloroacetate (15.0 g) was added after 12 h. Subsequently, the mixture was cooled down at room temperature and inorganic salt

was filtrated (139.7 g) and washed with acetone. The filtrate and acetone from the washing process were combined and acetone was distilled off with other volatile fractions up to 150 °C under nitrogen. Acetic acid (746 ml) and 430.6 g of ammonium acetate were added to the dark liquid distilling residue. The mixture was kept under reflux with stream of nitrogen at 120 °C for 4 h. Ninety-eight grams (yield 43%) of a product was obtained by filtration from the mixture after the cooling. A sample for analysis was recrystallized from ethylacetate. The melting point was 176–179 °C. NMR data **I**: ^{1}H NMR (360 MHz, DMSO) 1.07 (3H, t, $J = 8.6$ Hz, CH_3); 3.35 (2H, d, $J = 8.6$ Hz, CH_2); 3.98 (2H, q, $J = 8.6$ Hz, CH_2); 7.40–7.47 (3H, m, Ar*H*); 7.54–7.58 (2H, m, Ar*H*); 10.64 (1H, s, N*H*).

MS analysis, $M = 231$.

4.2.2. Ethyl-1,1′-biphenyl-4-carboxylate

1,1′-Biphenyl-4-carboxylic acid (19.8 g, 0.1 mol), ethanol (60 ml, 0.5 mol), and sulphuric acid (2 ml) were added to the two-necked flask with thermometer and refluxing condenser and stripped. The reaction mixture was refluxed for 10 h and after that a mixture was cooled. The arisen product was filtrated. Recrystallization was performed in ethanol. The amount of product obtained was 9.4 g (yield 67%). The melting point was 47.5–48 °C.

4.2.3. Ethyl-3-(1,1′-biphenyl-4-yl)-3-oxopropanoate

The mixture of hydridosodium (1.9 g, 0.08 mol), ethyl-1,1′-biphenyl-4-carboxylate (18.1 g, 0.08 mol) and 1-butoxybutane (40 ml) was added to the two-necked flask with thermometer and refluxing condenser and stripped. The reaction mixture was heated to 100 °C and ethylacetate (3.52 g, 0.04 mol) in 1-butoxybutane (10 ml) was added to the mixture for about 100 min. After cooling down diethylether (100 ml) was added to reaction mixture. The obtained salt was filtrated and acidified by hydrogen chloride to pH 5. The product was filtrated and washed with water. The melting point was 74–76 °C. The amount of product obtained was 17.3 g (80.7% yield).

*4.2.4. Ethyl-4,5-dihydro-5-oxo-2-(1,1′-biphenyl-4-yl)-(1H)pyrrole-3-carboxylate (**II**)*

Ethyl-3-(1,1′-biphenyl-4-yl)-3-oxopropanoate (41.08 g, 0.15 mol) and ethylbromoacetate (26.08 g, 0.15 mol) with sodium carbonate (22.72 g), 30.1 ml acetone, 337.3 ml ethyleneglycol dimethylether were added to the three-necked flask with thermometer and refluxing condenser and stripped by stream of nitrogen. The reaction mixture was refluxed for 10 h. Acetone was continuously added to the reaction mixture to keep the constant volume due to evaporating off. Subsequently, the mixture was cooled down at room temperature and inorganic salt was filtrated and washed with acetone. The filtrate and acetone from the washing process were combined and acetone was distilled off with other volatile fractions up to 150 °C under nitrogen. Acetic acid (119.4 ml) and 68.88 g of ammonium acetate were added to the dark liquid distilling residue. The mixture was kept under reflux with stream of nitrogen at 120 °C for 4 h. Seventeen grams (yield 35%) of a product was obtained by filtration from the mixture after the cooling. The melting point was 153–158 °C.

Elemental analysis: Calculated: C (74.25), H (5.58), N (4.56); Found: C (74.24), H (5.84), N (4.58). NMR data **II**: ^{1}H NMR (500 MHz, DMSO) 1.17 (3H, t, $J = 7.1$ Hz, CH_3); 4.08 (2H, q, $J = 7.1$ Hz, CH_2); 7.46 (1H, t, H_{para}); 7.55 (2H,t, H_{meta}); 7.79 (2H, m, H_{ortho}); 7.79 and 7.73 (4H, m, 1,4 disubstituted phenyl ring); 10.76 (1H, s, N*H*).

MS analysis, $M = 307$. Positive-ion MS: *m/z* 308 $[M + H]^+$, 100%. Negative-ion MS: *m/z* 306 $[M - H]^-$, 100%.

*4.2.5. Ethyl-4,5-dihydro-5-oxo-2-phenyl-4-(phenylmethylidene)-(1H)pyrrole-3-carboxylate (**Ia**)*

Toluene (35 ml), 2.31 g (0.01 mol) starting material (**I**) and 1.06 g (0.01 mol) benzaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (ca. 0.3 ml). The product was filtrated and dried. Yellow compound (**Ia**) (1.9 g, 60% yield), m.p. 200–205 °C was obtained by recrystallization (200 ml, *n*-hexane:acetone (2:3)).

Elemental analysis: Calculated: C (75.25), H (5.33), N (4.39); Found: C (75.31), H (5.55), N (4.43). NMR data **Ia**: ^{1}H NMR (500 MHz, DMSO) 1.06 (3H, t, $J = 7.1$ Hz, CH_3); 4.11 (2H, q, $J = 7.1$ Hz, CH_2); 7.47–7.54 (6H, m, Ar*H*); 7.60 (2H, d, $J = 6.8$ Hz, Ar*H*); 8.07 (1H, s, –C*H*=); 8.21–8.23 (2H, m, Ar*H*); 11.03 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO) 13.7; 59.6; 103.3; 127.9; 128.2; 129.0; 129.0; 130.1; 130.2; 130.3; 131.5; 134.3; 140.0; 150.9; 163.3; 166.6.

MS analysis, $M = 319$. Positive-ion MS: *m/z* 320 $[M + H]^+$, 100%; *m/z* 274 $[M + H - C_2H_5OH]^+$. Negative-ion MS: *m/z* 318 $[M - H]^-$, 100%; *m/z* 272 $[M - H - C_2H_5OH]^-$.

*4.2.6. Ethyl-4,5-dihydro-5-oxo-2-(1,1′-biphenyl-4-yl)-4-(phenylmethylidene)-(1H)pyrrole-3-carboxylate (**IIa**)*

Toluene (24.5 ml), 2.1 g (0.007 mol) starting material (**II**) and 0.7 g (0.007 mol) benzaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.2 ml). The product was filtrated and dried. Yellow compound (**IIa**) (2 g, 74% yield), m.p. 205–210 °C, was obtained by recrystallization (200 ml, *n*-hexane:acetone (2:3)).

Elemental analysis: Calculated: C (78.97), H (5.35), N (3.54); Found: C (78.9), H (5.35), N (3.75). NMR data (*Z*)-**IIa**: ^{1}H NMR (500 MHz, DMSO) 1.12 (3H, t, $J = 6.8$ Hz, CH_3); 4.16 (2H, q, $J = 6.8$ Hz, CH_2); 7.46–7.83 (12H, m, Ar*H*); 8.07 (1H, s, Ar-C*H*=); 8.23 (2H, m, Ar*H*); 11.10 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO) 13.8, 59.7; 103.5; 126.1, 126.8; 128.1, 128.2, 128.3, 129.1, 129.2, 129.4, 129.8, 131.6, 139.3, 140.0 (Ar-C*H*=);141.8, 150.4, 163.4, 166.6. (*E*)-**IIa**: ^{1}H NMR (500 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IIa**) 0.67 (3H, t, $J = 6.8$ Hz, CH_3); 3.69 (2H, q, $J = 6.8$ Hz, CH_2); 7.58 (1H, s, Ar-C*H*=); 11.06 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IIa**) 13.1, 60.3; 104.3; 126.5, 126.9, 128.9,

129.2, 129.8, 130.6, 134.6 (Ar-C*H*=); 135.7, 139.1, 142.2, 149.8, 164.3, 168.6.

MS analysis, $M = 395$. Positive-ion MS: *m/z* 396 $[M + H]^+$, 100%; *m/z* 350 $[M + H\text{-}C_2H_5OH]^+$. Negative-ion MS: *m/z* 394 $[M - H]^-$, 100%.

*4.2.7. Ethyl-4,5-dihydro-5-oxo-2-phenyl-4-(4-biphenylmethylidene)-1H-pyrrole-3-carboxylate (**Ib**)*

Toluene (35 ml), 2.31 g (0.01 mol) starting material (**I**) and 1.82 g (0.01 mol) 4-biphenyl-carboxyaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.3 ml). The product was filtrated, washed with 100 ml toluene and dried. Orange compound (**Ib**) (3 g, 76% yield) with m.p. 209–213 °C was obtained.

Elemental analysis: Calculated: C (79.00), H (5.31), N (3.54); Found: C (79.78), H (5.48), N (3.62). NMR data (*Z*)-**Ib**: ^{1}H NMR (500 MHz, DMSO) 1.07 (3H, t, $J = 6.8$ Hz, C*H*$_3$); 4.12 (2H, q, $J = 6.8$ Hz, C*H*$_2$); 7.40–7.63 (8H, m, Ar*H*); 7.83 (4H, m, Ar*H*); 8.11 (1H, s, Ar-C*H*=); 8.37 (2H, m, Ar*H*); 11.09 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO) 13.7; 59.6; 103.5; 126.4; 126.8; 128.0; 128.1; 129.0; 129.1; 129.2; 130.2; 130.4; 132.5; 133.6; 139.4, 139.5 (Ar-C*H*=); 141.7; 150.7; 163.4; 166.7. (*E*)-**Ib**: ^{1}H NMR (500 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**Ib**) 0.68 (3H, t, $J = 6.8$ Hz, C*H*$_3$); 3.77 (2H, q, $J = 6.8$ Hz, C*H*$_2$); 7.64 (1H, s, Ar-C*H*=); 11.03 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**Ib**) 13.0; 60.3; 104.3; 134.2 (Ar-C*H*=); 141.0; 150.5; 164.2; 168.7.

MS analysis M = 395. Positive-ion MS: *m/z* 396 $[M + H]^+$, 100%; *m/z* 350 $[M + H\text{–}C_2H_5OH]^+$. Negative-ion MS: *m/z* 394 $[M - H]^-$, 100%; *m/z* 348 $[M - H - C_2H_5OH]^-$.

*4.2.8. Ethyl-4,5-dihydro-5-oxo-2-(1,1′-biphenyl-4-yl)-4-(4-biphenylmethylidene)-(1H)pyrrole-3-carboxylate (**IIb**)*

Toluene (17.5 ml), 1.54 g (0.005 mol) starting material (**II**) and 1.27 g (0.005 mol) 4-biphenyl-carboxyaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.2 ml). The product was filtrated, washed with 100 ml toluene and dried. Orange compound (**IIb**) (2 g, 85% yield) with m.p. 290–296 °C was obtained.

Elemental analysis: Calculated: C (81.51), H (5.34), N (2.97); Found: C (81.51), H (5.48), N (3.01). NMR data: dissoluble in DMSO for NMR analysis.

MS analysis $M = 471$. Positive-ion MS: *m/z* 472 $[M + H]^+$, 100%. Negative-ion MS: *m/z* 470 $[M - H]^-$, 100%.

*4.2.9. Ethyl-4,5-dihydro-5-oxo-2-phenyl-4-(1-naphthalenylmethylidene)-(1H)pyrrole-3-carboxylate (**Ic**)*

Toluene (35 ml), 2.31 g (0.01 mol) starting material (**I**) and 1.56 g (0.01 mol) 1-naphthtylaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.3 ml). The product was filtrated, washed with 100 ml toluene and dried. Orange compound (**Ic**) (1.7 g, 46% yield) with m.p. 193–196 °C was obtained.

Elemental analysis: Calculated: C (78.06), H (5.15), N (3.79); Found: C (78.65), H (5.35), N (3.84). NMR data (*Z*)-**Ic**: ^{1}H NMR (500 MHz, DMSO) 1.10 (3H, t, $J = 6.8$ Hz, C*H*$_3$); 4.15 (2H, q, $J = 6.8$ Hz, C*H*$_2$); 7.50–7.68 (8H, m, Ar*H*); 8.05 (3H, m, Ar*H*); 8.20 (1H, m, Ar*H*); 8.67 (1H, s, Ar-C*H*=); 10.99 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO) 14.2; 59.9; 103.1; 124.2; 125.6; 126.5; 127.4; 128.3; 128.7; 129.2; 129.6; 130.1; 130.6; 130.7; 130.8; 131.3; 131.7, 133.5; 137.1 (Ar-C*H*=); 152.6; 163.7; 166.9. (*E*)-**Ic**: ^{1}H NMR (500 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (Z)-**Ic**) 0.29 (3H, t, $J = 6.8$ Hz, C*H*$_3$); 3.25 (2H, q, $J = 6.8$ Hz, C*H*$_2$); 7.64 (1H, s, Ar-C*H*=); 11.06 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**Ic**) 12.7; 59.9; 104.4; 132.2 (Ar-C*H*=); 150.2; 163.9; 168.2.

MS analysis $M = 369$. Positive-ion MS: *m/z* 370 $[M + H]^+$, 100%; *m/z* 324 $[M + H - C_2H_5OH]^+$. Negative-ion MS: *m/z* 368 $[M - H]^-$, 100%; *m/z* 322 $[M - H - C_2H_5OH]$.

*4.2.10. Ethyl-2-(1,1′-biphenyl-4-yl)-5-oxo-4,5-dihydro-4-(1-naphthalenylmethylidene)-(1H)pyrrole-3-carboxylate (**IIc**)*

Toluene (35 ml), 3.1 g (0.01 mol) starting material (**II**) and 1.56 g (0.01 mol) 1-naphthtylaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.3 ml). The product was filtrated, washed with 100 ml toluene and dried. Orange compound (**IIc**) (1.7 g, 61% yield) with m.p. 201–206 °C was obtained.

Elemental analysis: Calculated: C (80.88), H (5.20), N (3.14); Found: C (81.04), H (5.31), N (3.38). NMR data: (*Z*)-**IIc**: ^{1}H NMR (500 MHz, DMSO) 1.16 (3H, t, $J = 6.8$ Hz, C*H*$_3$); 4.20 (2H, q, $J = 6.8$ Hz, C*H*$_2$); 7.46–8.08 (14H, m, Ar*H*); 8.68 (1H, s, Ar-C*H*=); 8.23 (2H, m, Ar*H*); 11.04 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO) 13.9, 59.7, 102.8, 123.8, 125.2, 126.0, 126.1, 126.5, 127.0, 128.2, 128.4, 128.8, 129.1, 129.2, 129.8, 130.0, 130.3, 131.00, 131.4, 133.1, 136.7, 139.3, 142.0, 151.7, 163.4, 166.6. (*E*)-**IIc**: ^{1}H NMR (500 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IIc**) 0.30 (3H, t, $J = 6.8$ Hz, C*H*$_3$); 3.27 (2H, q, $J = 6.8$ Hz, C*H*$_2$); 11.11 (1H, s, N*H*). ^{13}C NMR (125 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IIc**) 12.7, 59.9; 104.5; 124.6, 125.3, 126.9, 127.1, 127.3, 128.1, 128.6, 129.20, 129.50, 131.1, 132.2, 133.3, 139.1, 142.2, 149.6, 164.0, 168.2.

MS analysis $M = 445$. Positive-ion MS: *m/z* 446 $[M + H]^+$, 100%; *m/z* 400 $[M + H - C_2H_5OH]^+$. Negative-ion MS: *m/z* 444 $[M - H]^-$, 100%.

*4.2.11. Ethyl-4,5-dihydro-5-oxo-2-phenyl-4-[[4-(dimethylamino)phenyl]methylidene]-1H-pyrrole-3-carboxylate (**Id**)*

Toluene (35 ml), 2.31 g (0.01 mol) starting material (**I**) and 1.49 g (0.01 mol) *p*-dimethylamino-benzaldehyde were added

to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.3 ml). The product was filtrated, washed with 100 ml toluene and dried. Red compound (**Id**) (2.9 g, 80% yield) with m.p. 231–234 °C was obtained.

Elemental analysis: Calculated: C (72.94), H (6.07), N (7.73); Found: C (73.16), H (6.32), N (7.70). NMR data **Id**: ^{1}H NMR (500 MHz, DMSO) 1.06 (3H, t, $J = 7.2$ Hz, CH_3); 3.09 (6H, s, −N−CH_3); 4.10 (2H, q, $J = 7.2$ Hz, CH_2); 6.80 (2H, d, $J = 9.1$ Hz, ArH); 7.46–7.52 (3H, m, ArH); 7.53–7.57 (2H, m, ArH); 7.95 (1H, s, −CH=); 8.38 (2H, d, $J = 9.1$ Hz, ArH); 10.85 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO) 13.7; 39.7; 59.4; 104.1; 111.1; 122.6; 123.2; 127.9; 129.0; 129.5; 130.9; 134.7; 141.5; 146.3; 151.9; 163.8; 166.7.

MS analysis $M = 362$. Positive-ion MS: m/z 363 $[M + H]^+$, 100%; m/z 317 $[M + H - C_2H_5OH]^+$. Negative-ion MS: m/z 361 $[M - H]^-$, 100%.

*4.2.12. Ethyl-4,5-dihydro-5-oxo-2-(1,1′-biphenyl-4-yl)-4-[[4-(dimethylamino)phenyl]methylidene]-(1H)pyrrole-3-carboxylate (**IId**)*

Toluene (17.5 ml), 1.54 g (0.005 mol) starting material (**II**) and 0.75 g (0.005 mol) *p*-dimethylamino-benzaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.2 ml). The product was filtrated, washed with 100 ml toluene and dried. Red compound (**IId**) (2.2 g, 82% yield) with m.p. 282–288 °C was obtained.

Elemental analysis: Calculated: C (76.69), H (5.98), N (6.39); Found: C (76.88), H (6.53), N (6.39). NMR data (*Z*)-**IId**: ^{1}H NMR (500 MHz, DMSO) 1.11 (3H, t, $J = 6.8$ Hz, CH_3); 4.14 (2H, q, $J = 6.8$ Hz, CH_2); 3.10 (6H, s, N(CH_3)$_2$); 6.81 (2H, m); 7.45 (1H, ''t'', ArH); 7.54 (2H, ''t'', ArH); 7.65 (2H, ''d'', ArH); 7.80 (4H, m, ArH); 7.94 (1H, s, Ar-CH=); 8.40 (2H, m, ArH); 10.91 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO) 13.9, 39.7, 59.6, 104.3, 111.2, 122.6, 123.3, 126.1, 126.8, 128.1, 129.2, 129.7, 129.8, 134.9, 139.4, 141.1, 141.5, 145.7, 152.0, 163.9, 166.8. (*E*)-**IId**: ^{1}H NMR (500 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IId**) 0.81 (3H, t, $J = 6.8$ Hz, CH_3); 3.90 (2H, q, $J = 6.8$ Hz, CH_2); 10.85 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IId**) and that for N(CH_3)$_2$ by the solvent: 13.3, 60.4, 105.1, 111.4, 122.5, 123.6, 126.4, 126.8, 128.0, 128.1, 128.3, 128.6, 132.6, 136.2, 139.2, 141.6, 146.4, 151.4, 165.1, 169.0.

MS analysis $M = 438$. Positive-ion MS: m/z 439 $[M + H]^+$, 100%. Negative-ion MS: no signal.

*4.2.13. Ethyl-4,5-dihydro-5-oxo-2-phenyl-4-[[4-(carbonyl)phenyl]methylidene]-1H-pyrrole-3-carboxylate (**Ie**)*

Toluene (35 ml), 2.31 g (0.01 mol) starting material (**I**) and 1.34 g (0.01 mol) terephthaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.3 ml). The product was filtrated, washed with 100 ml toluene and dried. Red compound (2.2 g) was obtained. Based on MS analysis final product was the mixture of **Ie** and other product. A raw sample was added to 200 ml acetone, than it was heated under reflux and filtrated. The filtrate was concentrated using rotary evaporator and the obtained compound was filtrated off. The orange compound (**Ie**) was obtained by recrystallization from acetone. The process of isolation was checked using TLC analysis (mobile phase: acetone:*n*-hexane (2:3), thin layer: Alugram Sil G/UV, R_f (**Ie**) = 0.4, R_f (other product) = 0). Melting point was 215–219 °C.

Elemental analysis: Calculated: C (72.64), H (4.90), N (4.03); Found: C (74.04), H (4.93), N (3.91). NMR data **Ie**: ^{1}H NMR (500 MHz, DMSO) 1.07 (3H, t, $J = 6.8$ Hz, CH_3); 4.11 (2H, q, $J = 6.8$ Hz, CH_2); 7.52–7.58 (3H, m, ArH); 7.59–7.63 (2H, m, ArH); 7.98 (2H, d, $J = 7.8$, ArH); 8.08 (1H, s, −CH=); 8.30 (2H, d, $J = 7.8$ Hz, ArH); 10.09 (1H, s, −CH=O) 11.11 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO) 13.7; 60.3; 103.1; 127.9; 129.0; 129.0; 130.1; 130.3; 131.1; 131.6; 136.3; 137.7; 140.0; 152.6; 163.1; 166.4; 192.6.

MS analysis $M = 347$. Positive-ion MS: m/z 348 $[M + H]^+$, 100%; m/z 302 $[M + H - C_2H_5OH]^+$. Negative-ion MS: m/z 346 $[M - H]^-$, 100%; m/z 300 $[M - H - C_2H_5OH]^-$.

*4.2.14. Ethyl-4,5-dihydro-5-oxo-2-(1,1′-biphenyl-4-yl)-4-[[4-(carbonyl)phenyl]methylidene]-(1H)pyrrole-3-carboxylate (**IIe**)*

Toluene (35 ml), 3.07 g (0.01 mol) starting material (**II**) and 1.34 g (0.01 mol) terephthaldehyde were added to 100 ml volumetric flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (c. 0.3 ml). The product was filtrated, washed with 100 ml toluene and dried. Red compound (2.7 g) was obtained. A raw sample was added to 200 ml toluene, than it was heated under reflux and filtrated. The filtrate was concentrated using rotary evaporator and the obtained compound was filtrated off. The red compound (**IIe**) was obtained by recrystallization from toluene. Melting point was in the range 236–241 °C.

Elemental analysis: Calculated: C (76.58), H (5.00), N (3.31); Found: C (76.58), H (5.12), N (3.50). NMR data (*Z*)-**IIe**: ^{1}H NMR (500 MHz, DMSO) 1.12 (3H, t, $J = 6.8$ Hz, CH_3); 4.16 (2H, q, $J = 6.8$ Hz, CH_2); 7.44–7.99 (11H, m, ArH); 8.08 (1H, s, Ar-CH=); 8.31 (2H, m, ArH); 10.09 (1H, s, CHO); 11.20 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO) 13.8, 59.8, 103.3, 126.1, 126.9, 128.3, 129.0, 129.1, 129.2, 129.9, 131.2, 131.8, 136.4, 137.8, 139.2, 140.0, 142.1, 152.1, 163.2, 166.5, 192.6. (*E*)-**IIe**: ^{1}H NMR (500 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IIe**) 0.67 (3H, t, $J = 6.8$ Hz, CH_3); 3.69 (2H, q, $J = 6.8$ Hz, CH_2); 7.64 (1H, s, Ar-CH=); 10.08 (1H, s, CHO); 11.16 (1H, s, NH). ^{13}C NMR (125 MHz, DMSO, characteristic resonances, other signals were overlapped by those belonging to (*Z*)-**IIe**) 13.1, 60.2, 103.9, 126.4, 126.8, 127.9, 128.2, 129.5, 130.3, 130.7, 132.7, 135.9, 139.0, 141.6, 142.4, 163.8, 168.5, 192.7.

MS analysis $M = 423$. Positive-ion MS: m/z 424 $[M + H]^+$, 100%. Negative-ion MS: m/z 422 $[M - H]^-$, 100%.

5. Conclusions

Ten 2-aryl-4-arylmethylidene-pyrrolin-5-ones were synthesized by a condensation of various aromatic aldehydes with pyrrolinone esters with moderate reaction yields. All compounds were synthesized as *Z*-isomers. Their absorption spectra depend on a size of π-electronic system and polar substituents on arylmethylidene part. Excited state deactivation is a result of a competition between *E*–*Z* isomerisation and fluorescence that is preferred in rigid frozen solution.

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