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Structure, Z/E photoisomerization and an effect of (phenylene-)vinylene conjugation extension on absorption and fluorescence of methylidene-pyrrolinones

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HIGHLIGHTS

- ▶ Methylidene-pyrrolinones with extended conjugation chains were synthesized.
- ▶ Structures were estimated by X-ray diffraction.
- ▶ Structural changes upon Z/E photoisomerization were studied by NMR and DFT.
- ▶ N-methylated derivatives show solid-state fluorescence.

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ABSTRACT

Six methylidene-pyrrolinones with a conjugation chain extended by vinylene and phenylene-vinylene groups were studied; five of them were synthesized for the first time. Their structures were estimated theoretically by density functional theory (DFT) and proved by X-ray diffraction techniques in two cases. Structural changes upon Z/E photoisomerization in solution were studied by a combination of ^{1}H NMR spectroscopy and DFT GIAO method. Both types of conjugation extension caused a bathochromic shift in absorption. Vinylene extension produced the compounds fluorescent in solution. N-methylated derivatives have shown solid-state fluorescence.

1. Introduction

Ethyl 5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (pyrrolinone ester, Scheme 1) is an interesting intermediate in colorant syntheses. Due to strongly activated methylene group in position 4, it can undergo base catalyzed reaction with aromatic nitriles [1,2], a condensation with aromatic aldehydes [3–5], carboxy esters and chlorides [6], azo-coupling with diazonium salts [7–10] and oxidative dimerization [1,4]. The reaction with various aromatic nitriles catalyzed by *t*-amyl alcoholate gives usually asymmetrical diketo-pyrrolo-pyrroles (DPP) [11–13]. The exception is the reaction with *trans* cinnamonitrile, for which an addition on double C═C bond is preferred giving cyclopenta-pyrrolinones [2]. The products of piperidine catalyzed condensation of (substituted) benzaldehydes with pyrrolinone ester are (substituted) phenyl-methylidene-pyrrolones (compound **1**) [5].

The aim of the presented work was to study whether the reaction of *trans* cinnamaldehyde with pyrrolinone ester under piperidine catalysis involves also an addition on C═C bond or the condensation is preferred. As expected, the reaction conditions allowed only the condensation forming compound **2** (Scheme 1).

The role of side carboxyester group in position 3 of methylidene-pyrrolinone ring is crucial for final structure. Compound **1** arises from a reaction solely as the *Z* isomer, i.e. with *EE* arrangement of its 1,4-diphenyl-butadiene (**DPB**) hydrocarbon backbone [5], on the contrary to 3-unsubstituted methylidene-pyrrolinones with *EZ* **DPB** backbone [14]. Compound **1** easily undergoes *Z*/*E* photoisomerization [5]. The X-ray structures of 3-methylester analogues of **1** (*E* isomer) and **1m** (*Z* isomer) are known [15].

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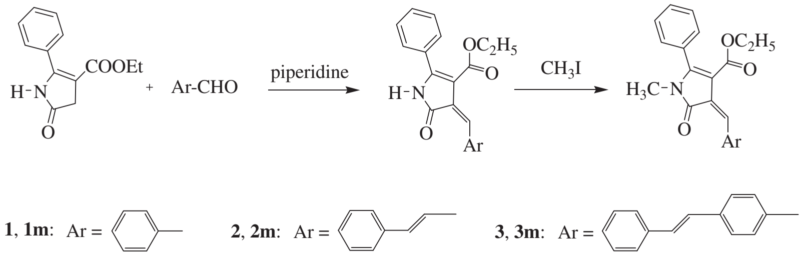


Scheme 1. Syntheses of the compounds under study.

Consequently, the second aim of the presented work was to study the structural details of **2**, including its eventual photoisomer(s). In order to make this study more general, we synthesized also another derivative with two exocyclic C=C double bonds of a different type (compound **3**). The effect of vinylene (**1** → **2**) and phenylene-vinylene (**1** → **3**) conjugation extension on absorption and fluorescence was evaluated both on compounds **1–3** and their *N*-methylated (**1m–3m**) derivatives (Scheme 1).

2. Experimental and theoretical procedures

2.1. Syntheses and analyses

The synthesis of **1** was reported previously [5], other five compounds synthesized according to Scheme 1 are new, so they were fully characterized. Compounds **2** and **3** arose solely as *Z* isomers on newly formed exocyclic double bond as confirmed by ^{3}J(^{13}C, ^{1}H) coupling constants on methylidene proton (Table 2) in the same way as for **1** [5]. The *trans* isomer on the C=C double bonds coming from cinnamaldehyde and stilbene-4-carbaldehyde remained unchanged during syntheses and *N*-methylation had no effect on the arrangements on both C=C bonds.

Table 1
Crystallographic data for **1m** and **2**.

Compound	**1m**	**2**
Empirical formula	$C_{21}H_{19}NO_3$	$C_{22}H_{19}NO_3$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P-1$
a (Å)	10.2600(5)	10.7030(8)
b (Å)	11.4941(7)	12.2839(8)
c (Å)	17.7968(8)	15.4090(10)
α (°)	90	103.264(5)
β (°)	123.886(5)	109.141(6)
γ (°)	90	102.715(5)
Z	4	4
V (Å^3)	1742.29(19)	1764.1(2)
D_c (g cm^{-3})	1.271	1.300
Crystal size (mm)	0.37 × 0.23 × 0.20	0.38 × 0.37 × 0.24
Crystal shape	Block	Block
μ (mm^{-1})	0.085	0.087
F[000]	704	728
h; k; l range	−12, 13; −14, 14; −22, 22	−13, 13; −14, 15; −19, 18
θ Range (°)	2.24–26.7	1.48–27.30
Reflections measured	20,674	30,256
Independent [R_{int}][a]	3656	7823
Observed [$I > 2\sigma(I)$]	2348	5062
Parameters refined	226	469
Max/min $\Delta\rho$ (eÅ^{-3})	0.719/−0.385	0.264/−0.327
GOF[b]	1.031	1.176
R[c]/wR[c]	0.1031/0.2484	0.0698/0.1300

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$.

[b] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{differs} - N_{params})]^{1/2}$.

[c] Weighting scheme: $w = \left[\sigma^2(F_o^2) + (w_1P)^2 + w_2P\right]^{-1}$, where $P = \left[\max(F_o^2) + 2F_c^2\right]$, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w\left(F_o^2\right)^2)]^{1/2}$.

2.1.1. Synthesis of ethyl (4Z)-5-oxo-2-phenyl-4-aryl-4,5-dihydro-1H-pyrrole-3-carboxylates (**2** and **3**)

Toluene (75 ml), ethyl 5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (pyrrolinone ester; 15 mmol) and aromatic aldehyde (15 mmol) were added into round bottom flask. The reaction mixture was heated under reflux for 4 h in the catalytic presence of piperidine (cca. 0.5 ml). The product was filtrated and dried.

2.1.2. Ethyl (4Z)-5-oxo-2-phenyl-4-[(2E)-3-phenylprop-2-en-1-ylidene]-4,5-dihydro-1H-pyrrole-3-carboxylate (**2**)

After recrystallization in mixture n-hexane: acetone (3:2) was obtained product with 56% yield with m.p. 220–223 °C. Elemental analysis: Calculated: C (76.50), H (5.54), N (4.06), Found: C (76.43), H (5.35), N (3.96). MS analysis *M* = 345. Positive-ion MS: *m*/*z* 346 [M+H]$^+$, 100%; *m*/*z* 300 [M+H-C2H5OH]$^+$.

2.1.3. Ethyl (4Z)-2-phenyl-5-oxo-4-{4-[(E)-2-phenylethenyl]benzylidene}-4,5-dihydro-1H-pyrrole-3-carboxylate (3)

Recrystallization was performed in methanol and product was obtained with 36% yield. The melting point was 224–227 °C. Elemental analysis: Calculated: C (79.79), H (5.50), N (3.32), Found: C (79.76), H (5.62), N (3.24). MS analysis *M* = 421. Positive-ion MS: *m*/*z* 422 [M+H]$^+$, 100%.

2.1.4. Synthesis of N-methylated derivatives (**1m–3m**)

DMF (60 ml), starting non-methylated compound (3 mmol) and potassium carbonate (4.2 mmol) were given to the three-necked flask with thermometer and refluxing condenser. After 20 min of stirring was added iodomethane (18 mmol). The reaction mixture was heated to 80 °C for 2 h. Product was isolated by precipitation to 50 ml distilled water and was filtered off.

2.1.5. Ethyl (4Z)-4-benzylidene-1-methyl-5-oxo-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**1m**)

Product was obtained with 95% yield. The melting point was 125–128 °C. Elemental analysis: Calculated: C (75.66), H (5.74), N (4.20), Found: C (75.41), H (5.59), N (4.12). MS analysis *M* = 333. Positive-ion MS: *m*/*z* 334 [M+H]$^+$, 100%.

2.1.6. Ethyl (4Z)-1-methyl-5-oxo-2-phenyl-4-[(2E)-3-phenylprop-2-en-1-ylidene]-4,5-dihydro-1H-pyrrole-3-carboxylate (**2m**)

Product was obtained with 94% yield. The melting point was 177–179 °C. Elemental analysis: Calculated: C (76.86), H (5.89), N (3.90), Found: C (75.87), H (5.67), N (3.81). MS analysis *M* = 359. Positive-ion MS: *m*/*z* 360 [M+H]$^+$, 100%; *m*/*z* 314 [M+H-C_2H_5OH]$^+$.

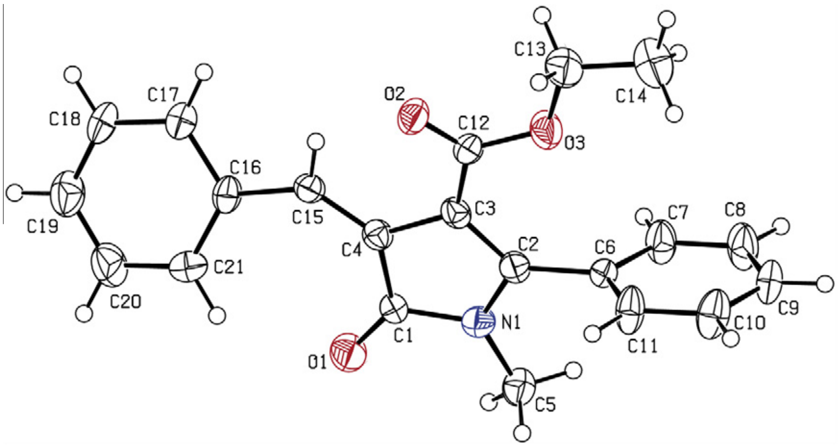


Fig. 1. The molecular structure (ORTEP 40% probability level) of **1m**. Selected interatomic distances (Å) and angles (°): O1—C1 1.223(5), O2—C12 1.210(5), O3—C12 1.318(5), O3—C13 1.448(6), C1—N1 1.399(5), N1—C2 1.367(6), C2—C3 1.403(6), C3—C4 1.458(6), C4—C1 1.485(6), C4—C15 1.349(6), C15—C16 1.465(6), C4—C15—C16 134.5(4), C1—C4—C3 106.1(3), C1—N1—C2 111.1(3).

*2.1.7. Ethyl (4Z)-1-methyl-5-oxo-4-{4-[(E)-2-phenylethenyl]benzylidene}-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**3m**)*

Product was recrystallized from methanol. 1.37 g (yield 66%) of a product was obtained. The melting point was 132–135 °C. Elemental analysis: Calculated: C (79.98), H (5.79), N (3.22), Found: C (79.71), H (5.85), N (3.13). MS analysis *M* = 435. Positive-ion MS: *m*/*z* 436 $[M+H]^+$, 100%.

2.2. Instrumental equipment

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400.13 MHz for ^{1}H, and 100.62 MHz for ^{13}C) in DMSO-d_6. The ^{1}H and ^{13}C chemical shifts were referenced to internal TMS (δ = 0.00). All 2D experiments (gradient-selected gs-COSY, gs-HMQC, gs-HMBC) were performed using manufacturer's software (Topspin 2.1).

The X-ray data for crystals of **1m** (yellow) and **2** (orange) were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [16]. The absorption was corrected by integration methods [17]. Structures were solved by direct methods (Sir92) [18] and refined by full matrix least-square based on F^2 (SHELXL97) [19]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C—H = 0.96 Å, 0.97, 0.93 and 0.93 Å for methyl, methylene, vinylidene hydrogen atoms and atoms in aromatic rings, respectively, and 0.86 Å for N—H bonds.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 827776 and 827777 for **1m** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

2.3. Quantum chemical calculations

The theoretical calculation based on density functional theory (DFT) were carried out. The geometry was optimized using B3LYP functional in combination with 6-311G(d,p) basis set. The same functional and basis set was used for gauge-including atomic orbital (GIAO) NMR computations. Solvent effect on chemical shifts was not taken into account. Absolute shielding for reference TMS computed at the same level of theory was 32.00.

Time dependent (TD) DFT calculations of excitation energies were carried out with the same XC functional and the broader basis set 6-311+G(2d,p). Solvent effect was taken into account through non-equilibrium polarized continuum model (PCM).

All calculation codes came from Gaussian03W program suite [20].

3. Results and discussion

3.1. Molecular and crystal structure

Single crystals of **1m** and **2** were of sufficient quality for X-ray diffraction techniques (Table 1). The only molecular structure of **1m** is shown on Fig. 1. On the contrary to **1m**, there were found two structures in a crystal cell of **2** (Fig. 2). The distance of the suggested double bond C2═C3 in **1m** and **2** (1.403(6) for **1m** and 1.368(3) and 1.372(3) Å for **2**) is significantly elongated when compared to the standard C═C distance (1.331 Å) [21], which is a proof of a conjugation within the central ring. Furthermore, compounds **1m** and **2** each display a shortening of the N1—C1 and N1—C2 bond distances (1.399(5), 1.367(6) Å for **1m** and 1.373(3), 1.392(3) and 1.368(3), 1.394(3) Å for both independent molecules of **2**), with respect to the standard N(sp^3)—C(sp^2) distance of 1.44 Å [21], attributable to a peptide-like bonding character. *Z* (**1m**), resp. *EZ* (**2**) arrangement on exocyclic C═C double bonds was confirmed. Side carboxyester group is in *s-trans* conformation in both cases. Both structures of **2** show similar rotation of 2-phenyl out of pyrrolinone ring (37–38°), which is considerably increased (79°) by a steric effect of *N*-methyl group in **1m**. Opposite pendant phenyl is almost coplanar with methylidene-pyrrolinone ring in a structure A of compound **2**, while considerably deviated from planarity in a structure B (16°) and especially in compound **1m** (23°), proving a remarkable influence of crystal packing forces on a planarity of chain conjugated systems. Torsion of carbonyl group out of pyrrolinone plane lies in an interval 13–19°.

There were detected two dimer-forming specific intermolecular interactions in a crystal of compound **2** (Fig. 3). First, A and B molecules are connected by two CO-HN hydrogen bonds with a length about 1.96–1.99 Å, i.e. a bit longer than a similar type of H-bond in the simplest DPP pigment (C.I.P.R.255) with the H-bond (O—H) length about 1.82 Å [22]. Second, two A molecules (but not B) are π–π stacked with the interplane distance about 3.18–3.19 Å.

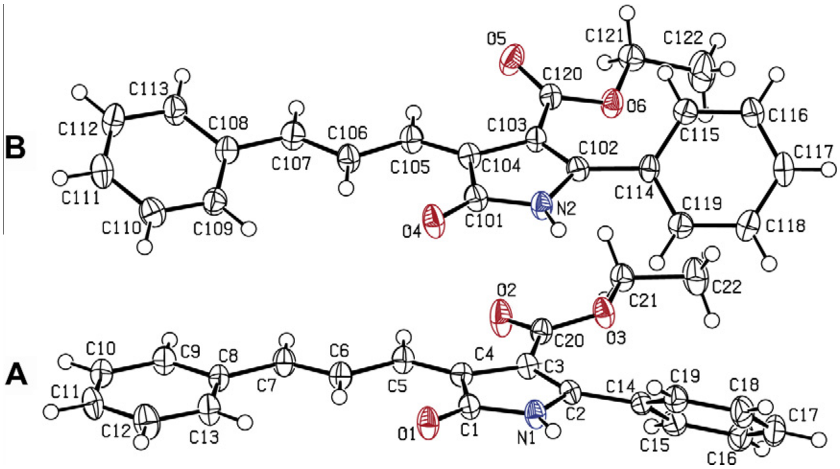
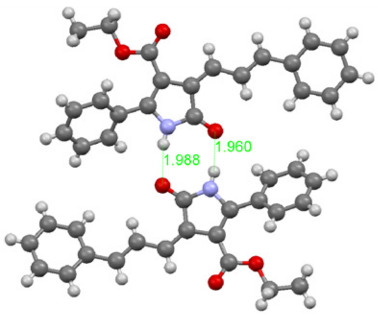
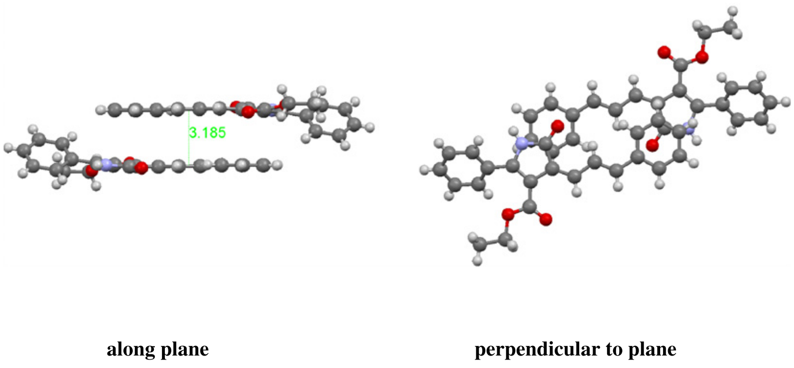


Fig. 2. The molecular structure (ORTEP 50% probability level) of **2**. Selected interatomic distances (Å) and angles (°): for molecule A: O1—C1 1.232(3), O2—C20 1.211(3), O3—C20 1.338(3), O3—C21 1.453(3), C1—N1 1.373(3), N1—C2 1.392(3), C2—C3 1.368(3), C3—C4 1.460(3),C4—C1 1.484(4), C4—C5 1.358(4), C5—C6 1.430(4), C6—C7 1.342(4), C7—C8 1.463(3); C4—C5—C6 125.1(2), C5—C6—C7 123.1(2), C6—C7—C8 125.9(2), C1—C4—C3 105.5(2), C1—N1—C2 111.7(2); for molecule B: O4—C101 1.231(3), O5—C120 1.209(3), O6—C120 1.340(3), O6—C121 1.452(3), C101—N2 1.368(3), N2—C102 1.394(3), C102—C103 1.372(3), C103—C104 1.459(3), C104—C101 1.488(4), C104—C105 1.359(4), C105—C106 1.435(4), C106—C107 1.338(4), C107—C108 1.465(4); C104—C105—C106 124.9(3), C105—C106—C107 122.9(3), C106—C107—C108 125.4(3), C101—C104—C103 105.5(2), C101—N2—C102 111.8(2).

(a) H-bond dimer



(b) л–stacked dimer



along plane **perpendicular to plane**

Fig. 3. The dimers in crystal of compound **2**. (a) The H-bond dimer of A and B molecules, (b) the π–π stacked dimer of two A molecules.

Although the lateral displacement (Fig. 3b) is considerable, this interaction is responsible for planarization of A molecule of **2**, on the contrary to B molecule of **2** and all molecules of **1m**, in which crystal no such specific intermolecular interactions were found.

3.2. *Z*/*E* photoisomerization in solution

Standing of DMSO-d_6 solutions of all six compounds under study on daylight for 1 week brought only one new set of proton signals in each case, i.e. only one new isomer arised in the compounds with two exocyclic C=C double bonds (**2**, **2m**, **3**, **3m**). Evaluation of ^{13}C and ^{1}H chemical shifts established, that all changes correspond to *Z*/*E* isomerization on methylidene-pyrrolinone C=C bond as for **1** and **1m**. Fig. 4 shows convincingly that the splitting pattern of the key proton H-4-2′ (=CH—CH=CH—) in the ^{1}H NMR spectrum does not change after irradiation and, thus, the mutual *all-trans* proton arrangement must be same both in *EZ*-**2m** and *EE*-**2m**. Full assignment can be found in Table 2. *Trans* arrangement

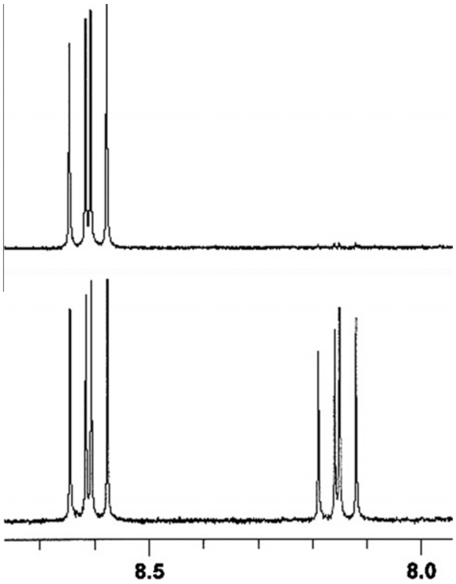


Fig. 4. A part of ^{1}H NMR spectrum showing the signal of H-4-2′ (=CH—CH=CH—) proton in compound *EZ*-**2m** (upper trace) and signals of H-4-2′ protons in a mixture of compounds *EZ*-**2m** and *EE*-**2m** formed after irradiation (bottom trace). ^{1}H chemical shifts are given in ppm.

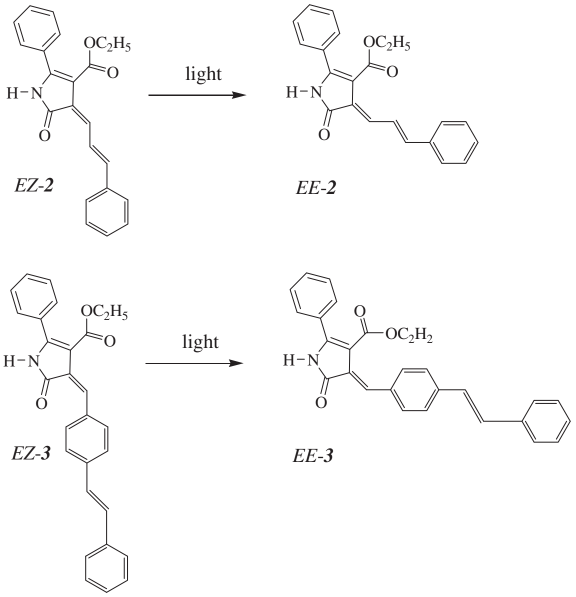
Table 2
^{1}H and 13C chemical shifts and ^{n}J(^{13}C, ^{1}H) and ^{n}J(^{1}H, ^{1}H) coupling constants (Hz, ±0.3 Hz) of compounds *EZ*-**2m** and *EE*-**2m** measured in hexadeuteriodimethyl sulfoxide.

H/C no.	*EZ*-**2m**			*EE*-**2m**		
	δ(^{1}H)	δ(^{13}C)		δ(^{1}H)	δ(^{13}C)	
2	–	153.5		–	155.2	
3	–	103.0	4.5 (CH)[a]	–	104.3	9.4 (CH)[a]
4	–	125.7		–	125.3	
5	–	166.4	12.0 (CH)[a], 2.5 (CH_3) [a]	–	167.9	6.8 (CH)[a], 2.8 (CH_3)[a]
NCH_3	2.903	27.5		2.906	28,0	
2-1′	–	130.4		–	130.5	
2-2′	7.51	129.2		c	129.2	
2-3′	7.57	128.2		c	128.3	
2-4′	7.51	129.7		c	129.7	
3-COO	–	162.7	2.8 (CH_2)[a]	–	163.6	2.8 (CH_2)[a]
OCH_2	3.966	59.2		3.968	59.8	
CH_3	0.92	13.6		0.80	13.4	
4-1′	7.90	139.8	11.9[b], 0.9[b]	7.40	135.6	12.0[b], 0.9[b]
4-2′	8.59	124.7	15.6[b], 11.9[b]	8.15	125.9	15.1[b], 12.0[b]
4-3′	7.32	143.9	15.6[b]	7.37	144.2	15.1[b]
4-4′	–	136.4		–	136.3	
4-5′	7.66	127.7		c	127.5	
4-6′	7.51	129.2		c	129.2	
4-7′	7.43	129.7		c	129.7	

[a] ^{n}J(^{13}C, ^{1}H).
[b] ^{n}J(^{1}H, ^{1}H).
[c] Strong overlap of proton signals in the range of 7.62–7.42 ppm.

of X—C_6H_4—CH=CH—Ph protons was retained after irradiation as clear from the practically same ^{3}J(^{1}H, ^{1}H) coupling constants in compounds **3** and **3m** being 15.3 ± 0.1 Hz. Definitely, photochemical isomerization undergoes according to Scheme 2, no side reaction to *ZZ* isomer or consecutive (photo)isomerization to *ZE* isomer was detected.

There was shown on pyrrolinone ester based hydrazone dyes [9], that the change in *Z*/*E* arrangement can force the side ester group to conformational change (*s-trans*/*s-cis*). So the recently validated combined experimental/theoretical procedure [9] was applied to a model set of six methylidene-pyrrolinones. In the first



Scheme 2. Photochemical *Z*/*E* isomerization.

Table 3
Theoretical relative ground state energies (E_{rel} [kcal mol^{-1}]) and ^{1}H chemical shifts of methyl (δ(CH_3)) and methylene (δ(CH_2)) protons together with their experimental values.

Compound	Isomer[a]	Conformer[b]	Theoretical			Experimental	
			E_{rel}[c]	δ(CH_3)[d]	δ(CH_2)[e]	δ(CH_3)	δ(CH_2)
1	*Z*	*s-trans*	0.000	0.905	4.103	1.06	4.11
		s-cis	1.060	1.525	4.203		
	E	*s-trans*	4.670	0.948	4.013	0.66	3.66
		s-cis	2.384	0.494	3.668		
1m	*Z*	*s-trans*	0.000	0.660	3.917	0.86	3.95
		s-cis	1.662	1.473	4.083		
	E	*s-trans*	4.730	0.637	3.739	0.57	3.58
		s-cis	3.219	0.401	3.586		
2	*Z*	*s-trans*	0.000	0.697	3.901	0.92	3.97
		s-cis	0.487	1.440	4.057		
	E	*s-trans*	2.334	0.622	3.915	0.81	3.97
		s-cis	3.974	1.252	4.118		
2m	*Z*	*s-trans*	0.000	0.948	4.095	1.11	4.12
		s-cis	1.097	1.487	4.166		
	E	*s-trans*	2.139	0.828	4.084	1.03	4.12
		s-cis	4.551	1.262	4.207		
3	*Z*	*s-trans*	0.000	0.911	4.115	1.07	4.12
		s-cis	1.054	1.519	4.206		
	E	*s-trans*	5.031	0.966	4.046	0.71	3.77
		s-cis	2.706	0.550	3.743		
3m	*Z*	*s-trans*	0.000	0.673	3.916	0.88	3.96
		s-cis	1.686	1.492	4.085		
	E	*s-trans*	5.079	0.631	3.754	0.62	3.68
		s-cis	3.570	0.503	3.644		

[a] On methylidene-pyrrolinone C=C bond.
[b] With respect to carboxy ester group.
[c] Value 0.000 kcal mol^{-1} was ascribed to the most stable isomer/conformer.
[d] Arithmetic mean of values for three protons.
[e] Arithmetic mean of values for two protons.

step the structure of both experimentally found isomers (*Z* and *E* for **1** and **1m**, resp. *EZ* and *EE* for **2**, **2m**, **3** and **3m**) each with both possible conformations of side carboxy ester group was optimized using by DFT and the relative ground state energies with respect to the most stable isomer/conformer were summarized in Table 3. The calculated structures of **1** and **2** are shown on Figs. 5 and 6 for illustration. *Z* isomers for all six compounds are always more stable than *E* isomers irrespective to carboxy ester conformation. More stable conformations of *Z* isomer are *s-trans* for all six

Table 4
Theoretical excitation energies of the first two $\pi\pi^*$ transitions (converted to λ_{00}) of *Z* isomers in *s-trans* conformation together with experimental absolute absorption and fluorescence maxima in DMSO at room temperature.

	PCM (DMSO) TD-DFT						Experimental			
	S_0–S_1			S_0–S_2			Absorption		Fluorescence	
	λ_{00}	f_{osc}	Coeff.	λ_{00}	f_{osc}	Coeff.	λ_{abs}	ε_{max}	λ_{emis}	Stokes
1	421	0.179	0.63 (1-1′)	352	0.663	0.18 (1-1′)	412	11,900	–	–
1m	421	0.343	0.62 (1-1′)	326	0.026	0.53 (2-1′)	409	8700	–	–
2	472	0.987	0.62 (1-1′)	356	0.335	0.63 (2-1′)	434	22,800	575	5650
2m	462	0.752	0.62 (1-1′)	359	0.610	0.65 (2-1′)	435	20,200	587	5950
3	488	1.527	0.70 (1-1′)	396	0.117	0.68 (2-1′)	435	30,000	–	–
3m	476	1.308	0.70 (1-1′)	399	0.311	0.68 (2-1′)	429	25,300	–	–

λ_{abs} (nm) – measured absolute absorption maxima.
ε_{max} (l mol^{-1} cm^{-1}) – measured molar absorptivity.
λ_{emis} (nm) – fluorescence emission maximum.
Stokes (cm^{-1}) – Stokes shift.
λ_{00} (nm) – computed excitation energy converted to wavelength.
f_{osc} – computed oscillator strength of 0–0 vibronic band.
Coeff. – expansion coefficient of the monoexcited configurations in TD DFT.

compounds (confirmed by X-ray for **1m** and **2**), while *s-cis* conformation is more probable for *E* isomer of **1**, **1m**, **3** and **3m**, but not for **2** and **2m**. Finally, the thermodynamical viewpoint prefers the conformational change after isomerization for the derivatives with phenyl ring bonded directly to methyliden-pyrolinone. These compounds could be thus interesting in photoswitching [23], if e.g. reesterified with a suitable biopolymer.

Only one value of ^{1}H chemical shift was found experimentally for two (three) methylene (methyl) protons of ethyl group, which means that a free rotation of ethyl on the NMR time scale must exist. On the other hand, the different average values of $\delta(CH_3)$, resp. $\delta(CH_2)$, for both isomers prove the stabilized position of the whole carboxy ester group. The chemical shifts (Table 4) computed by GIAO method are generally very similar for *s-trans*, resp. *s-cis*, conformers of both isomers, proving that ^{1}H chemical shifts of ethyl protons depend only on a conformation of carbethoxy group with respect to pyrrolinone ring. Finally, a considerable difference between the experimental values for both isomers must mean, that the conformation of carboxy ester is different for them, and vice-versa. The sets of theoretical values of methyl and methylene ^{1}H chemical shifts match the experimental ones significantly better for the most stable arrangement (Table 4). Theoretical values of methyl protons are systematically underestimated by 0.11–0.22 ppm, while the deviation of theoretical chemical shifts of methylene protons is only −0.01 to 0.07 ppm. Relatively small disagreement goes probably on account to imperfect theoretical methodology; any other assignment gives generally less consistent set of results. Thus, we consider the photochemical isomerizations in Scheme 2 including the conformation of carboxy ester group definitely proved. The *s-trans* arrangement of carboxyester group is more stable than the *s-cis* one in all cases, when this group is more or less coplanar with pyrrolinone ring. This is the case of isomers with *Z* arrangement on methylidene-pyrrolinone double bond for all six compounds. The sterical interaction of the vinylene

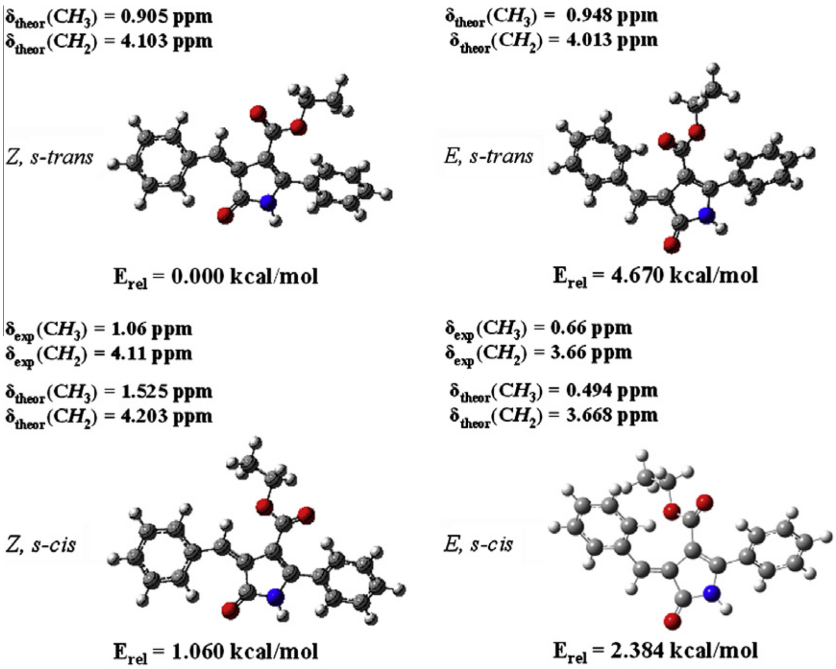


Fig. 5. DFT computed structure of **1** with both conformations of carbethoxy group of *E* and *Z* isomers, together with relative total energies and GIAO NMR and experimental ^{1}H chemical shifts of the methylene and methyl groups.

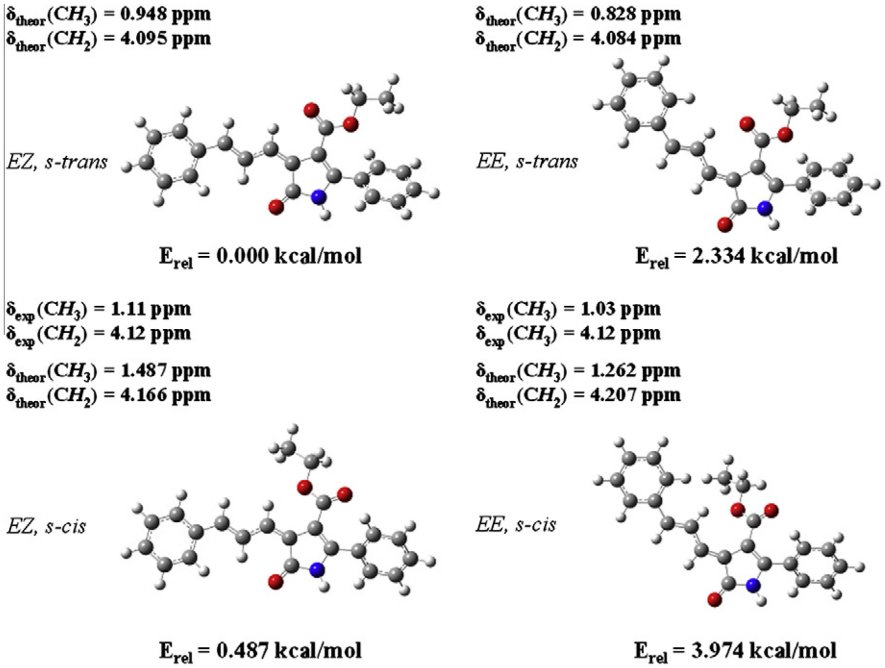


Fig. 6. DFT computed structure of **2** with both conformations of carbethoxy group of *E* and *Z* isomers, together with relative total energies and GIAO NMR and experimental ^{1}H chemical shifts of the methylene and methyl groups.

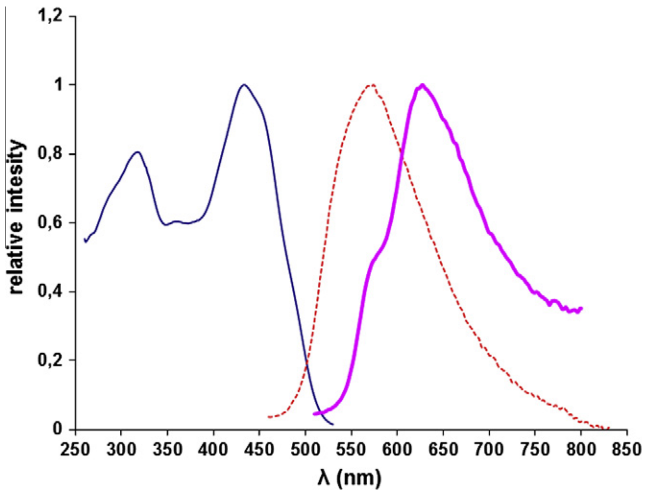


Fig. 7. Absorption (left) and fluorescence (middle) of **2** in DMSO and its fluorescence in polycrystalline solid-state (right).

protons with these oxygens in *E* isomers of compounds **2** (Fig. 6) and **2m** also leaves the carboxy ester group almost coplanar. On the contrary, the interation with *ortho*-phenyl hydrogens in *E* isomers of **1** (Fig. 5), **1m**, **3** and **3m** forces carboxy ester group to rotate out-of-plane considerably. This type of sterical hindrance is the driving force of the conformational change upon photoisomerization.

3.3. Absorption and fluorescence

Both vinylene and phenylene-vinylene conjugation extension causes a comparable bathochromic and hyperchromic shift in absorption (Table 4). PCM TD DFT theoretical computations predict a considerably higher red shift; the disagreement may go on account to the fact, that for all compounds the absorption maximum does not correspond to 0–0 vibronic transition, but to the higher one (Fig. 7 for illustration). Compounds **2** (Fig. 7) and **2m** are the only fluorescent ones in solution (Table 4). Their ability of fluorescence may relate to the sterically less demanding intramolecular reorganization in excited state, not leading to conformational change of 3-ethylester group. Stokes shift is relatively high in both cases (Table 4), mainly because the absorption/fluorescence maxima do not correspond to 0–0 vibronic transitions, so the reabsorption should not affect the eventual application.

On the contrary, four of six derivatives (**1m**, **2**, **2m** and **3m**) are able to fluoresce strongly in polycrystalline solid-state, in which the competitive photoisomerization is limited, with the emission maxima at 561, 630, 577 and 608 nm, respectively. The presence of solid-state (ss) fluorescence makes the compounds interesting for some applications, but the interpretation of this phenomenon is not straightforward [24]. A bit simplifying, the ss fluorescence was expected for all three *N*-methylated derivatives **1m–3m** by analogy with N-alkylated DPPs [25], in which H-bonding is disabled and π–π stacking is considerably limited by molecular non-planarity. But the appearance of ss fluorescence of compound **2** is a bit surprising, as both types of (usually quenching) dimers are present in its crystal (Fig. 3).

4. Conclusion

Ethyl 5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate was condensed with *trans* cinnamaldehyde and *trans* stilbene-4-carbaldehyde to give the dyes with vinylene (**2**) and phenylene-vinylene (**3**) conjugation extension with respect to parent ethyl 4-benzylidene-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**1**) arose from a reaction with benzaldehyde. All three dyes **1–3** were isolated solely in *Z* arrangement on a newly created exocyclic C=C double bond. Photochemical *Z*/*E* isomerization underwent exclusively on this bond, giving thus only *EE* isomers of **2** and **3**. Steric effect accompanying photoisomerization forced the molecule to change a conformation of 3-carboxy ester group from *s-trans* to *s-cis* in compounds **1** and **3**, but not in **2**. Absorption spectra of both extended compounds **2** and **3** are red shifted with respect to **1**. Compound **2** is able to fluoresce both in solution and in solid-state. *N*-methylated derivatives of **1–3** behave in a very similar way as their precursors with respect to *Z*/*E* photoisomerization and show solid-state fluorescence.

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