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Synthesis, structure, absorption and fluorescence of Pechmann dye heteroanalogues

Tarek Aysha [a,b,*], Stanislav Luňák Jr. [c], Antonín Lyčka [d,e], Jan Vyňuchal [f], Zdeněk Eliáš [a,f], Aleš Růžička [c], Zdeňka Padělková [c], Radim Hrdina [a]

[a] Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 95, CZ-53210 Pardubice, Czech Republic
[b] National Research Centre, Dokki, PO Box 12311, Cairo, Egypt
[c] Faculty of Chemical Technology, University of Pardubice, Studentská 95, CZ-53210 Pardubice, Czech Republic
[d] Research Institute for Organic Syntheses (VUOS), Rybitví 296, CZ-533 54 Pardubice, Czech Republic
[e] University of Hradec Králové, Faculty of Science, Rokitanského 62, CZ 500 03 Hradec Králové 3, Czech Republic
[f] Synthesia a.s., Pardubice, Semtín 103, CZ-532 17 Pardubice, Czech Republic

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ABSTRACT

Three *N*-analogues of Pechmann dye with identical aryl groups in the 5, 5′-positions (aryl = phenyl, 2-naphthyl, 2-thienyl) and carboxy ester groups in the 3,3′-positions were synthesized by oxidative dimerization of the corresponding 5-aryl-pyrrolinone esters. Derivatives with improved solubility in most organic solvents were prepared by subsequent N-methylation. The dyes were confirmed as *E* isomers, i.e. holding an all-*trans* 1,6-diaryl-1,3,5-hexatriene backbone, with slight torsion of central C=C bond by X-ray diffraction and density functional theory (DFT) calculations. No *E*/*Z* photoisomerization was observed. Full assignment of ^{1}H and ^{13}C NMR signals was performed. The absorption spectra are quite similar with the maxima in the range 572 nm (aryl = phenyl)–643 nm (aryl = 2-thienyl) in accordance with time dependent DFT calculations of excitation energies. No fluorescence was observed in solution, while all compounds fluoresce in low temperature solvent glass (77 K) and a weak solid-state fluorescence of phenyl and 2-naphthyl derivatives in red/IR region was detected.

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1. Introduction

Reinvestigation of established organic chromophores has resulted in such chromophores being employed as key components in organic electronic devices. Diketopyrrolopyrroles (DPPs), in which the (substituted) phenyl rings in the 3,6-positions are replaced by (substituted) thiophenes, form probably the most prominent class of dyes from this point of view. Considering only “small”, i.e. non-polymeric DPPs, their efficiencies as donors in bulk heterojunction (BHJ) organic photovoltaic cells (OPV) with C_{70} [1] or C_{60} [2] fullerene or alternative [3] acceptors are remarkable. Likewise, surprisingly high hole mobilities were found in a field-effect transistor (FET) device [4]. Such success stimulated a considerable effort to modify other classes of organic dyes and pigments to meet the specific requirements of a given technological area. Replacing or substituting phenyl rings with thiophenes was recently performed in e.g. quinacridones [5], isoindigos [6,7], benzodifuranones [8] and benzodipyrrolidones [9].

A thiophene-containing analogue of legendary of Pechmann dye (exo-dilactone) [10] was also recently presented [11]. These dyes are generally not very stable and undergo a rearrangement to *endo*-6,6-dilactones [11,12]. The only known way to prepare their isoindigoid *N*-analogues (*exo*-5,5-dilactams), i.e. by direct (alkyl) amination is somewhat controversial. Whilst no problems were mentioned in the patent literature [13], low yield and poor selectivity were reported in a scientific paper [14]. If the derivatives with carboxy ester substituents in the 3,3′-positions are considered, the situation is much more clear. Such Pechmann dye derivative was synthesized from a furanone ester using Lawesson’s reagent [15]. *N*-Analogue **1** of Pechmann dye (Scheme 2, Table 1) was obtained by oxidative dimerization of 5-phenyl–pyrrolinone ester under considerably milder reaction conditions [13,16]. The route to the corresponding thiophene-containing analogue of **1**, i.e. compound **2**, was recently reported in patents [17,18], describing the syntheses of 5-(thiophen-2-yl)-pyrrolinone ester.

Our interest in the dyes coming from pyrrolinone esters lead recently to the studies of their reactions with aromatic nitriles,

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* Corresponding author. Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 95, CZ-53210 Pardubice, Czech Republic.
E-mail address: tarekaysha@hotmail.com (T. Aysha).

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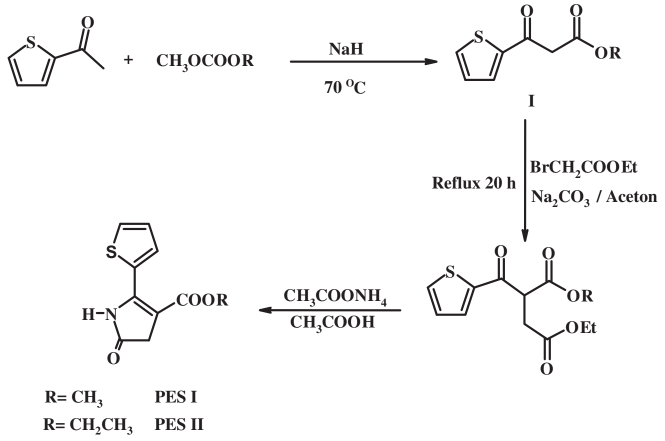


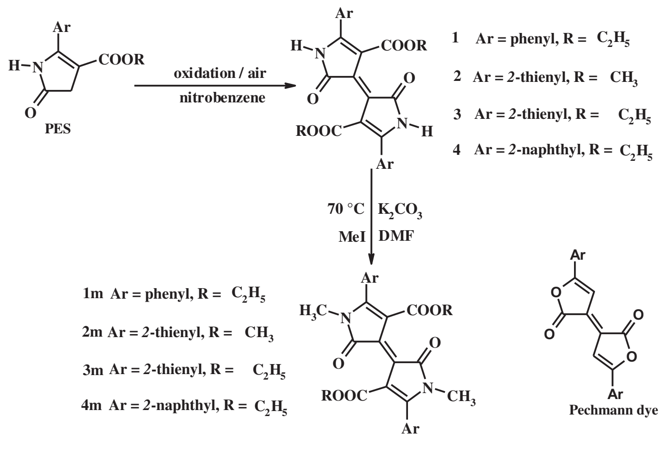
Scheme 1. Synthesis of thienyl derivatives of pyrrolinone esters.

leading to asymmetrical DPPs [19,20], condensations with aromatic aldehydes, leading to methylidene-pyrrolinones [21,22], and coupling with diazotized aromatic amines, forming hydrazones [23,24]. Consequently, we decided to prepare known parent compound **1** and report for the first time the thiophene containing analogues **2** and **3**, differing by ester group in the 3,3′-positions, and to study the relation between their structure and spectral properties by a combined experimental/theoretical approach. As these compounds are essentially insoluble, their more soluble *N*-methyl derivatives **1m**, **2m** and **3m** were also described. As a 2-naphthyl substituted pyrrolinone ester was available from our previous studies [23,24], we also synthesized the new compound **4** and its soluble derivative **4m** in order to study the effect of conjugation extension.

2. Experimental and computational procedures

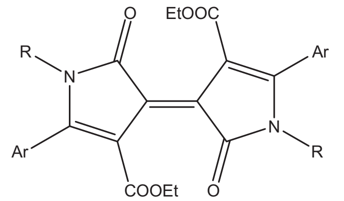
2.1. Quantum chemical calculations

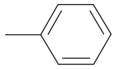
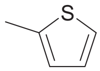
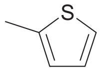
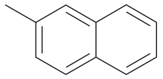
The ground state geometry of six compounds **1**–**3m** was optimized using quantum chemical calculations based on density functional theory (DFT). Hybrid three-parameter B3LYP functional in combination with 6-311G(d,p) basis set was used. No constraints were preliminarily employed, but, if the nonconstrained computations converged to symmetrical structures, the final computations were carried out with symmetry constraint. Practically, only symmetrical structures with an *E*-arrangement on the central double bond were investigated and C_2 symmetry constraint was applied in all cases. No imaginary frequencies were found by vibrational analysis, confirming that the computed geometries were real minima on the ground state hypersurfaces.



Scheme 2. Synthesis of *N*-analogues of Pechmann dyes and their *N*-methylated derivatives.

Table 1
Structure of prepared dyes.



Dye	Ar	R
1		H
1m		CH_3
2[a]		H
2m[a]		CH_3
3		H
3m		CH_3
4		H
4m		CH_3

[a] COOMe instead of COOEt in 3,3′ positions.

Time dependent (TD) DFT computations of the vertical excitation energies were carried out on the computed ground state geometries. The same exchange-correlation functional (B3LYP) was used with rather broader basis set (6-311+G(2d,p)). The solvent effect of DMSO was involved by non-equilibrium polarized continuum model (PCM). The same xc functional, but only 6-311G(d,p) basis set was used for the excited state TD DFT optimisation of model compound **1** with only hydrogens in the 3,3′-positions.

All methods were taken from Gaussian09W program suite [25], and the default values of computational parameters were used. The results were analysed using GaussViewW from Gaussian Inc.

2.2. Materials and equipments

2-Acetylthiophene (98%), sodium hydride (60% dispersion in mineral oil), anhydrous 1,2 dimethoxyethane (99.5%), dimethylcarbonate (98%), diethylcarbonate (98%) and ethyl bromoacetate (98%) were purchased from Sigma–Aldrich. Solvents for spectroscopic measurements (spectroscopic grade) were purchased from Fluka.

The absorption spectra were recorded at room temperature in DMSO using a Perkin–Elmer Lambda 35 spectrophotometer with 1 cm pathlength quartz cuvettes. A Perkin–Elmer (P.–E.) LS55 was used for measuring fluorescence spectra at low temperatures. 2-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 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.

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 to determine 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 analyser Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1000. The samples were dissolved in acetonitrile and analysed by direct infusion at the flow rate 100 μL min^{-1}. The selected precursor ions were further analysed by MS/MS analysis 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 mL min^{-1} and 45 psi, respectively.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. The samples were dissolved in hexadeuteriodimethyl sulfoxide. The ^{1}H and ^{13}C NMR chemical shifts were referenced to the central signal of the solvent ($\delta = 2.55$ and 39.6, respectively).

The X-ray data for crystals of **1m** and **2m** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [26]. The absorption was corrected by integration methods [27]. Structures were solved by direct methods (Sir92) [28] and refined by full matrix least-square based on F^2 (SHELXL97) [29]. 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 $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97 and 0.93 Å for methyl, methylene hydrogen atoms and atoms in aromatic rings, respectively. $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$, $GOF = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

Crystallographic data for **1m**: $C_{28}H_{26}N_2O_6$, $M = 486.51$ g/mol, monoclinic, $P2_1/c$, $a = 18.6501(12)$, $b = 7.5760(4)$, $c = 18.0710(10)$ Å, $\beta = 107.389(5)°$, $Z = 4$, $V = 2436.6(3)$ Å^3, $D_c = 1.326$ g cm^{-3}, $\mu = 0.094$ mm^{-1}, $T_{min}/T_{max} = 0.979/0.987$; $-24 \le h \le 24$, $-9 \le k \le 9$, $-23 \le l \le 21$; 16,414 reflections measured ($\theta_{max} = 27°$), 16,403 independent ($R_{int} = 0.0526$), 3553 with $I > 2\sigma(I)$, 325 parameters, $S = 1.210$, $R1$(obs. data) = 0.0595, $wR2$(all data) = 0.1082; max., min. residual electron density = 0.263, −0.322 e Å^{-3}.

Crystallographic data for **2m**: $C_{22}H_{18}N_2O_6S_2$, $M = 470.50$ g/mol, monoclinic, $P2_1/c$, $a = 13.0170(6)$, $b = 17.2491(10)$, $c = 9.8270(10)$ Å, $\beta = 111.703(5)°$, $Z = 4$, $V = 2050.0(3)$ Å^3, $D_c = 1.524$ g cm^{-3}, $\mu = 0.305$ mm^{-1}, $T_{min}/T_{max} = 0.942/0.973$; $-16 \le h \le 16$, $-22 \le k \le 22$, $-12 \le l \le 11$; 15,774 reflections measured ($\theta_{max} = 27.4°$), 15,558 independent ($R_{int} = 0.0674$), 3170 with $I > 2\sigma(I)$, 302 parameters, $S = 1.122$, $R1$(obs. data) = 0.0673, $wR2$(all data) = 0.1150; max., min. residual electron density = 0.355, −0.538 e Å^{-3}.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 912966 & 912967 for **1m** and **2m**, 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 www: http://www.ccdc.cam.ac.uk).

2.3. Syntheses and analytics

Starting pyrrolinone esters, ethyl 4,5-dihydro-5-oxo-2-phenyl(1*H*) pyrrole-3-carboxylate and ethyl-4,5-dihydro-5-oxo-2-naphthyl(1*H*) pyrrole-3-carboxylate were synthesized according to published procedures and melting points were similar as the reported ones as published [20,21].

Synthesis of thienyl pyrrolinone esters (PES I and PES II) based on using a corresponding β-ketoester I, methyl 3-oxo-3-(thiophen-2-yl) propanoate in the case of thienyl PES I and ethyl 3-oxo-3-(thiophen-2-yl) propanoate in the case of thienyl PES II were prepared as reported procedure [17,30].

2.3.1. Thienyl pyrrolinone esters

General procedure

Alkyl 3-oxo-3-(thiophen-2-yl) propanoate (β-ketoester I) (0.38 mol), ethyl bromoacetate (63.5 g, 0.38 mol), sodium carbonate (56 g, 0.53 mol), acetone (400 mL) and 1,2 dimethoxyethane (95 mL) were added to the three necked flask equipped with thermometer, stirrer and reflux condenser. The reaction mixture was heated under reflux for 20 h. Acetone was added to the reaction mixture to maintain a constant volume due to slight evaporation. The cooled mixture was filtered to remove inorganic salts which were 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 (285 mL, 5.0 mol) and ammonium acetate (163 g, 2.11 mol) were added to the dark residue. The mixture was kept under reflux at 120 °C for 4 h. The product was obtained by filtration from the mixture after cooling, then washed with boiling methanol and boiling water.

2.3.1.1. Methyl 5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (thienyl PES I). Greenish needle precipitate, 50% yield with mp = 221–223 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 3.56 (2H, s, CH_2), 3.68 (3H, s, CH_3), 7.22 (1H, dd, ^{3}J(H, H) = 5.0 Hz, ^{3}J(H, H) = 3.9 Hz, CH), 7.89 (1H, dd, ^{3}J(H, H) = 3.9 Hz, ^{4}J(H, H) = 1.2 Hz, CH), 7.93 (1H, dd, ^{3}J(H, H) = 5.0 Hz, ^{4}J(H, H) = 1.2 Hz, CH) three thiophene protons, 10.89 (1H, br.s, NH).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 30.2, 51.0, 100.7, 126.9, 129.6, 131.6, 132.5, 145.4, 163.4, 176.2.

MS analysis, $M = 223$ g/mol: positive-ion MS: m/z 224 $[M + H]^+$; m/z 192 $[M + H - CH_3OH]^+$ 100%, negative-ion MS: m/z 222 $[M - H]^-$ 100%; m/z 190 $[M - H - CH_3OH]^-$ 100%.

Elemental analysis; calculated ($C_{10}H_9NO_3S$): C (53.80%) H (4.06%) N (6.27%); found: C (54.40%) H (4.27%) N (6.17%).

2.3.1.2. Ethyl 5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (thienyl PES II). Yellowish precipitate, 54% yield with mp = 196–199 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.26 (3H, t, ^{3}J(H, H) = 7.1 Hz, CH_3), 3.45 (2H, s, CH_2), 4.17 (2H, q, ^{3}J(H, H) = 7.1 Hz, OCH_2), 7.23 (1H, dd, ^{3}J(H, H) = 5.0 Hz, ^{3}J(H, H) = 3.9 Hz, CH), 7.88 (1H, dd, ^{3}J(H, H) = 3.9 Hz, ^{4}J(H, H) = 1.2 Hz, CH), 7.93 (1H, dd, ^{3}J(H, H) = 5.0 Hz, ^{4}J(H, H) = 1.2 Hz, CH) three thiophene protons, 10.86 (1H, br.s, NH).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 14.4, 38.3, 59.6, 101.2, 126.9, 129.7, 131.9, 132.4, 145.2, 163.1, 176.3.

MS analysis, $M = 237$ g/mol: Positive-ion MS: m/z 238 $[M + H]^+$; m/z 192 $[M + H - C_2H_5OH]^+$ 100%, Negative-ion MS: m/z 236 $[M - H]^-$ 100%; m/z 190 $[M - H - C_2H_5OH]^-$ 100%.

Elemental analysis; Calculated ($C_{11}H_{11}NO_3S$): C (55.68%) H (4.67%) N (5.90%); Found: C (55.91%) H (4.78%) N (5.92%).

2.3.2. Synthesis of Pechmann dye analogues

General procedure

To 500 mL Keller flask equipped with stirrer, thermometer, refluxing condenser and capillary for air supply, nitrobenzene (275 mL), pyrrolinone ester (3.5 mmol) and sodium 9,10-anthraquinone-1,5-disulfonate (0.75 g, 1.82 mmol) were added. The reaction mixture was heated to 180 °C under intensive air bubbling and stirring. After 1 h of heating nitrobenzene was distilled off under reduced pressure and to the blue residual, n-hexane (230 mL) was added and the mixture was heated under reflux for 30 min. The product was filtrated while remaining hot and washed by 3 × 50 mL boiling methanol.

*2.3.2.1. Ethyl-4-[1,2-dihydro-4-(ethoxycarbonyl)-5-phenyl-2-oxo-3H-pyrrol-3-ylidene]-4,5-dihydro-2-phenyl-5-oxo-1H-pyrrole-3-carboxylate (**1**).* Preparative yield 69%, mp < 300 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.19 (6H, t, ^3J(H, H) = 7.1 Hz, 2 × CH_3), 4.16 (4H, q, ^3J(H, H) = 7.1 Hz, 2 × CH_2), 7.56 (4H, m, aromatic protons), 7.72 (6H, m, aromatic protons), 11.19 (2H, br.s, 2 × NH).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 14.0 (2 × CH_3), 60.3 (2 × CH_2), 108.7, 128.3, 128.7, 151.8 (2 × all C), 128.6, 128.8, 131.3 (2 × all CH), 164.2 (2 × COO), 168.2 (2 × C=O).

MS analysis, $M = 458$ g/mol: Positive-ion MS: m/z 459 $[M + H]^+$; m/z 413 $[M + H - C_2H_5OH]^+$ 100%, Negative-ion MS: m/z 457 $[M - H]^-$ 100%; m/z 411 $[M - H - C_2H_5OH]^-$ 100%.

Elemental analysis; Calculated ($C_{26}H_{22}N_2O_6$): C (68.11%), H (4.84%), N (6.11%); Found: C (67.88%), H (4.47%), N (6.11%).

*2.3.2.2. Methyl-4-[4-(methoxycarbonyl)-2-oxo-5-(thiophen-2-yl)-1,2-dihydro-3H-pyrrol-3-ylidene]-5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**2**).* Preparative yield 56%, mp < 300 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 3.74 (6H, s, 2 × CH_3), 7.30 (2H, dd, ^3J(H, H) = 5.0 Hz, ^3J(H, H) = 3.9 Hz, 2 × CH), 7.98 (2H, dd, ^3J(H, H) = 3.9 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH), 8.07 (2H, dd, ^3J(H, H) = 5.0 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH) six thiophene protons, 11.39 (2H, br.s, 2 × NH).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 51.5 (2 × CH_3), 107.3, 127.5, 129.9, 144.1 (2 × all C), 128.3, 132.8, 134.8 (2 × all CH), 164.7 (2 × COO), 167.7 (2 × C=O).

MS analysis, $M = 442$ g/mol: Positive-ion MS: m/z 443 $[M + H]^+$; m/z 396 $[M + H - CH_3OH]^+$ 100%, Negative-ion MS: m/z 441 $[M - H]^-$ 100%.

Elemental analysis; Calculated ($C_{20}H_{14}N_2O_6S_2$): C (54.29%), H (3.19%), N (6.33%); Found: C (55.01%), H (3.21%), N (6.50%).

*2.3.2.3. Ethyl-4-[4-(ethoxycarbonyl)-2-oxo-5-(thiophen-2-yl)-1,2-dihydro-3H-pyrrol-3-ylidene]-5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**3**).* Preparative yield 58%, mp < 300 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.27 (6H, t, ^3J(H, H) = 7.1 Hz, 2 × CH_3), 4.23(4H, q, ^3J(H, H) = 7.1 Hz, 2 × CH_2), 7.33 (2H, dd, ^3J(H, H) = 5.0 Hz, ^3J(H, H) = 3.9 Hz, 2 × CH), 7.96 (2H, dd, ^3J(H, H) = 3.9 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH), 8.06 (2H, dd, ^3J(H, H) = 5.0 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH) six thiophene protons, 11.35 (2H, br.s, 2 × NH).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 14.1 (2 × CH_3), 60.4 (2 × CH_2), 107.7, 127.4, 130, 143.9 (2 × all C), 128.2, 132.6, 134.6 (2 × all CH), 164.3 (2 × COO), 167.7 (2 × C=O).

MS analysis, $M = 470$ g/mol: Positive-ion MS: m/z 471 $[M - H]^+$ 100%; m/z 425 $[M + H - C_2H_5OH]^+$ 100%.

Elemental analysis; Calculated ($C_{22}H_{18}N_2O_6S_2$): C (56.16%) H (3.86%) N (5.95%); Found: C (56.51%), H (3.91%), N (5.94%).

*2.3.2.4. Ethyl-4-[1,2-dihydro-4-(ethoxycarbonyl)-5-(naphthalen-2-yl)-2-oxo-3H-pyrrol-3-ylidene]-4,5-dihydro-2-(naphthalen-2-yl)-5-oxo-1H-pyrrole-3-carboxylate (**4**).* Preparative yield 52%, a sample was purified by recrystallization from ethanol, mp < 300 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.21 (6H, t, ^3J(H, H) = 7.1 Hz, 2 × CH_3), 4.21 (4H, q, ^3J(H, H) = 7.1 Hz, 2 × CH_2), 7.67 (2H, m), 7.69 (2H, m), 7.72 (2H, m), 8.04 (2H, m), 8.06 (2H, m), 8.08 (2H, m), 8.38 (2H, m) fourteen naphthalene protons, 11.34 (2H, br.s, 2 × NH).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 14.0 (2 × CH_3), 60.3 (2 × CH_2), 109.2, 126.1, 128.3, 132.1, 133.9, 151.7 (2 × all C), 125.2, 127.8, 127.9, 128.0, 128.3, 128.9, 129.3 (2 × all CH), 164.3 (2 × COO), 168.2 (2 × C=O).

MS analysis, $M = 558$ g/mol: Positive-ion MS: m/z 559 $[M + H]^+$; m/z 513 $[M + H - C_2H_5OH]^+$ 100%, Negative-ion MS: m/z 557 $[M - H]^-$ 100%.

Elemental analysis; Calculated ($C_{34}H_{26}N_2O_6$): C (73.11%), H (4.69%), N (5.02%); Found: C (73.22%), H (4.85%), N (5.09%).

*2.3.2.5. Ethyl-4-[1,2-dihydro-4-(ethoxycarbonyl)-1-methyl-5-phenyl-2-oxo-3H-pyrrol-3-ylidene]-4,5-dihydro-1-methyl-2-phenyl-5-oxo-1H-pyrrole-3-carboxylate (**1m**).* DMF (60 mL), compound **1** (1.44 g, 3.14 mmol) and anhydrous potassium carbonate (0.6 g, 4.3 mmol) were added to the three-necked flask connected with thermometer and refluxing condenser. After 20 min of stirring, iodomethane (2.68 g, 8.84 mmol) was added. The reaction mixture was heated to 100 °C for 2 h. Coppery laminas in dark violet solution were obtained after precipitation by added distilled water (50 mL). Product was extracted from the mixture by ether (3 × 50 mL). Organic layer was isolated, additional ether (20 mL) was added and the product was filtered off. Acquired crystals were flushed by 15 mL of ether for removing mother liquor and dried. 0.3 g, 20% yield of the product was obtained, mp 198–202 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.03 (6H, t, ^3J(H, H) = 7.1 Hz, 2 × CH_3), 2.96 (6H, s, 2 × N-CH_3), 4.03 (4H, q, ^3J(H, H) = 7.1 Hz, 2 × CH_2), 7.53 (4H, m, aromatic protons), 7.71 (6H, m, aromatic protons).

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 13.9 (2 × CH_3), 28.1 (2 × N-CH_3), 60.0 (2 × CH_2), 109.0, 127.3, 129.4, 159.6 (2 × all C), 128.3, 128.4, 129.3 (2 × all CH), 163.3 (2 × COO), 166.6 (2 × C=O).

MS analysis $M = 486$ g/mol, Positive-ion MS: m/z 487 $[M + H]^+$, 100%; m/z 441 $[M + H - C_2H_5OH]^+$.

Elemental analysis; Calculated ($C_{28}H_{20}N_2O_6$): C (69.12%), H (5.39%), N (5.76%), Found: C (68.94%), H (5.21%), N (5.67%).

2.3.3. N-Alkylated Pechmann dye analogues **2m**–**4m**

General procedure

DMF (80 mL), corresponding Pechmann dye analogue (5.56 mmol) and anhydrous potassium carbonate (1.60 g, 11.3 mmol) were added to 250 mL three-necked flask connected with thermometer and reflux condenser. After 30 min of stirring at room temperature, iodomethane (6.32 g, 44.5 mmol) was added. The reaction mixture was heated to 65–70 °C for 1 h then the mixture was cooled down to room temperature then added to iced water (50 mL), ppt was filtrated off and washed with boiling water (150 mL).

*2.3.3.1. Methyl (4E)-4-[4-(methoxycarbonyl)-1-methyl-2-oxo-5-(thiophen-2-yl)-1,2-dihydro-3H-pyrrol-3-ylidene]-1-methyl-5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**2m**).* Dark blue precipitate with 91% yield was obtained, mp < 300 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 3.17 (6H, s, 2 × N-CH_3), 3.66 (6H, s, 2 × CH_3), 7.35 (2H, dd, ^3J(H, H) = 5.0 Hz, ^3J(H, H) = 3.8 Hz, 2 × CH), 7.74 (2H, dd, ^3J(H, H) = 3.8 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH), 8.07 (2H, dd, ^3J(H, H) = 5.0 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH) six thiophene protons.

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 28.9 (2 × N-CH_3), 51.6 (2 × CH_3), 109.5, 126.6, 127.7, 148.2 (2 × all C), 128.1, 1132.6, 33.4 (2 × all CH), 164.0 (2 × COO), 166.6 (2 × C═O).

MS analysis, $M = 470$ g/mol: Positive-ion MS: m/z 471 $[M + H]^+$; m/z 425 $[M + H - CH_3OH]^+$ 100%, Negative-ion MS: m/z 469 $[M - H]^-$ 100%.

Calculated ($C_{22}H_{18}N_2O_6S_2$): C (56.16%) H (3.86%) N (5.95%) Found: C (56.45%), H (3.91%), N (5.99%).

*2.3.3.2. Ethyl (4E)-4-[4-(ethoxycarbonyl)-1-methyl-2-oxo-5-(thiophen-2-yl)-1,2-dihydro-3H-pyrrol-3-ylidene]-1-methyl-5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**3m**).* Dark blue precipitate with 92% yield of the product was obtained, mp < 300 °C.

^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.16 (6H, t, ^3J(H, H) = 7.1 Hz, 2 × CH_3), 3.15 (6H, s, 2 × N-CH_3), 4.13 (4H, q, ^3J(H, H) = 7.1 Hz, 2 × CH_2), 7.35 (2H, dd, ^3J(H, H) = 5.0 Hz, ^3J(H, H) = 3.8 Hz, 2 × CH), 7.74 (2H, dd, ^3J(H, H) = 3.8 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH), 8.07 (2H, dd, ^3J(H, H) = 5.0 Hz, ^4J(H, H) = 1.2 Hz, 2 × CH) six thiophene protons.

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 14.1 (2 × CH_3), 28.8 (2 × N-CH_3), 60.5 (2 × CH_2), 110.1, 126.6, 127.9, 148.2 (2 × all C), 128.1, 132.5, 133.2 (2 × all CH), 163.6 (2 × COO), 166.6 (2 × C═O).

MS analysis, $M = 498$ g/mol: Positive-ion MS: m/z 499 $[M + H]^+$; m/z 453 $[M + H - C_2H_5OH]^+$ 100%, Negative-ion MS: m/z 497 $[M - H]^-$ 100%.

Calculated ($C_{24}H_{22}N_2O_6S_2$): C (57.82%) H (4.45%) N (5.62%); Found: C (57.91%), H (4.51%), N (5.60%).

*2.3.3.3. Ethyl-4-[1,2-dihydro-4-(ethoxycarbonyl)-1-methyl-5-(naphthalen-2-yl)-2-oxo-3H-pyrrol-3-ylidene]-4,5-dihydro-1-methyl-2-(naphthalen-2-yl)-5-oxo-1H-pyrrole-3-carboxylate (**4m**).* ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 1.01 (6H, t, ^3J(H, H) = 7.1 Hz, 2 × CH_3), 3.05 (6H, s, 2 × N-CH_3), 4.21 (4H, q, ^3J(H, H) = 7.1 Hz, 2 × CH_2), 7.68 (2H, m), 7.70 (2H, m), 7.72 (2H, m), 8.08 (2H, m), 8.10 (2H, m), 8.13 (2H, m), 8.27 (2H, m) fourteen naphthalene protons.

^{13}C NMR (100 MHz, DMSO-d6, δ, ppm): 14.0 (2 × CH_3), 28.3 (2 × N-CH_3), 60.0 (2 × CH_2), 109.3, 126.0, 130.0, 132.1, 133.5, 155.9 (2 × all C), 126, 127.1, 127.8, 128.0, 128.3, 128.7, 128.8 (2 × all CH), 163.4 (2 × COO), 166.7 (2 × C═O).

MS analysis, $M = 586$ g/mol: Positive-ion MS: m/z 587 $[M + H]^+$; m/z 541$[M + H - C_2H_5OH]^+$ 100%.

Elemental analysis; Calculated ($C_{36}H_{30}N_2O_6$): C (73.71%), H (5.15%), N (4.78%), Found: C (73.42%), H (5.30%), N (5.03%).

3. Results and discussions

3.1. Synthesis

The synthesis of various pyrrolinone esters (phenyl, 2-naphthyl) [20,21] commenced from β-ketoesters obtained through Claisen condensation of the corresponding esters. This method was not successful for thienyl derivatives, thus the β-ketoester of thienyl derivatives I were prepared by the reaction of 2-acetylthiophene with dimethylcarbonate in case of thienyl PES I or diethylcarbonate in the case of thienyl PES II in the presence of sodium hydride. The process was very efficient giving β-ketoester I with yields over 90% (Scheme 1) and the overall yield of thienyl pyrrolinone ester was higher than 50%. During the last amidation/cyclization step in syntheses of thienyl PES I (Scheme 1) ethanol was the only leaving product and no pyrrolinone ethyl ester was formed.

Four Pechmann dye analogues were successfully prepared by an oxidative dimerization of the corresponding pyrrolinone esters in the presence of air and nitrobenzene as a solvent with a good yield over 50% for all compounds (Scheme 2). Compounds **1**–**4** are highly insoluble in a variety of solvents and generally improved solubility was noted for their N-methyl derivatives **1m**–**4m** were prepared by N-methylation with methyl iodide using potassium carbonate as a base in DMF. The reaction yield was over 90% for all compounds except compound **1m** which was 20%.

3.2. X-ray diffraction and DFT calculated structures

Pechmann dye was established as the strictly planar *E* isomer (180°) both by X-ray diffraction [31] and our DFT B3LYP/6-311G(d,p) calculations. These calculations also give planar arrangement on the central *exo*-5,5-dilactam in its O → NH and NMe analogues, but the phenyl–pyrrolinone dihedral angle is 21° and 38° respectively. Substitution of the 3,3′ positions by ethyl ester groups (compound **1**) leads to planarity distortion on the central C═C bond (167°, resp. 168°) in a slightly more stable ($\Delta E = 0.39$ kcal.mol^{-1}) *s-trans* rotamer (carboxy ester rotated 115° out of pyrrolinone ring), resp. *s-cis* rotamer (carboxy ester rotated 39°). Sterical effect of carboxy ester groups also leads to an increase of phenyl–pyrrolinone rotation (35° and 38° for *s-trans* and *s-cis*, respectively). *N*, *N′*-Dimethylation (compound **1m**) essentially leaves both the central (167°, resp. 169°) and carboxy ester (117°, resp. 39°) torsions unaffected, but the rotations of the pendant phenyls are considerably bigger (50°, resp. 60° for the *s-trans*, resp. *s-cis* rotamer). The *s-trans* rotamer of **1m** with respect to carboxy ester orientation is the slightly more stable rotamer by theory ($\Delta E = 0.22$ kcal mol^{-1}).

Generally, the experimental molecular structure of **1m** obtained by single crystal X-ray diffractometry fully supports the DFT predictions. An agreement in central double bond torsion is absolute (167°), the molecule is found as an *s-trans* rotamer with respect to the asymmetrically rotated ester groups (120° and 131°) and with pendant phenyl groups rotated by 56° and 59° (Fig. 1).

Looking for the absolute energy minima with respect to possible conformations of four thienyl substituted compounds **2**, **2m**, **3** and **3m** was more exhaustive, as not only the minima with respect to *s-trans*/*s-cis* rotamerism of methyl (ethyl) carboxy ester, but also of thiophene *s-trans*/*s-cis* orientation relative to pyrrolinone had to be calculated, i.e. four optimisations for each of these four compounds were carried out. The trend is quite clear with respect to ester group orientation: *s-cis* arrangement (i.e. opposite to that of the phenyl substituted compounds **1** and **1m**) is strongly preferred (5.23–7.38 kcal mol^{-1}) for all four compounds **2**, **2m**, **3**, **3m** (i.e. irrespective of whether methyl or ethyl ester is in position 3, irrespective to N-methylation and irrespective to the orientation of thiophene ring). The *s-cis* rotamers with respect to thiophene arrangement are also preferred in all cases, but this type of rotamerism affects the total energy only moderately (1.78–2.27 kcal mol^{-1}). The most stable conformations of thienyl derivatives show more planar structures, as compared to phenyl substituted analogues (**1**, **1m**). Typically, the central bond torsion is 169–170° for all and thiophene torsions are about 29° for non-methylated (**2**, **3**) and 42° for *N*-methylated examples (**2m**, **3m**).

The comparison of theoretical geometry of compound **2m** with the data coming from X-ray diffractometry is not as straightforward as in the case of **1m**. First, **2m** crystallizes as a centrosymmetrical π–π stacked dimer with the interplane distance about 3.79 Å (Fig. 2) and a stacking interaction may partially deform a molecular structure, and, second, there is a conformational disorder on the pendant (unstacked) part of a molecule, where thiophenes in both *s-trans* and *s-cis* arrangement are present. Experiment confirms the preferred *s-cis* conformation of methyl ester substituent and, as in the case of **1m**, gives an absolute agreement with theory on central

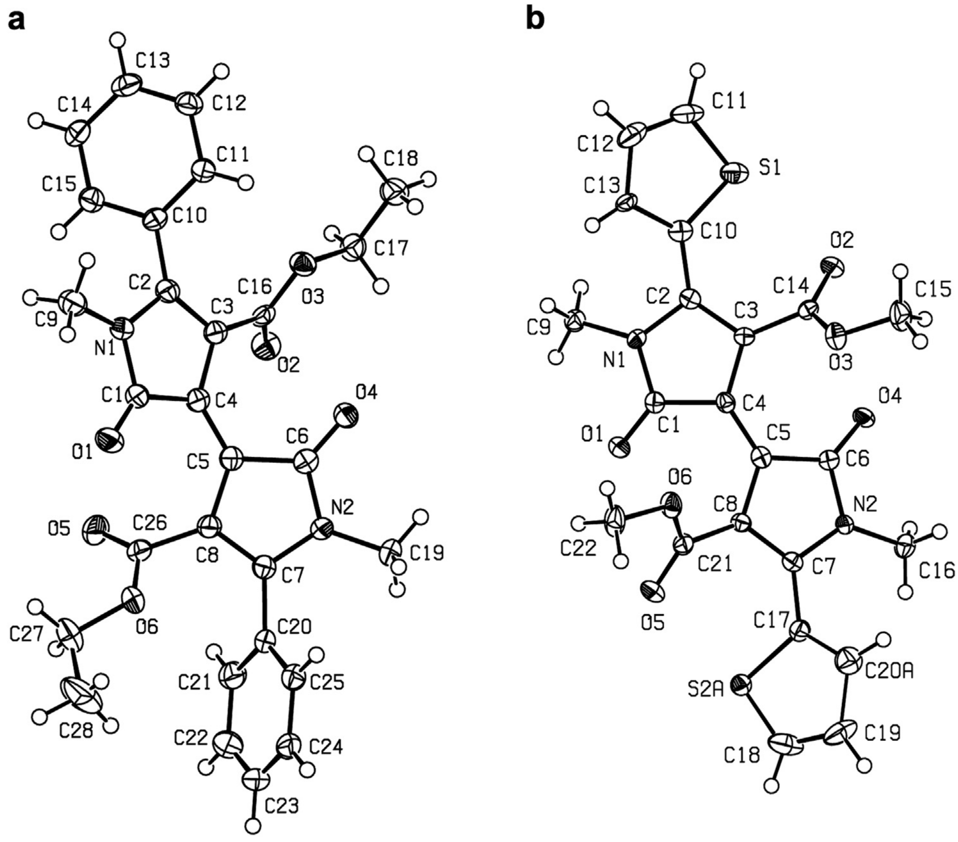


Fig. 1. The molecular structure (ORTEP 50% probability level) of compounds **1m** (a) and **2m** (b).

bond torsion angle (169°) for **2m**. On the other hand the theoretically preferred *s-cis* thiophene rotamer is not present in a stacked part of a molecular dimer and only partially present in a pendant part. Definitely, both rotamers should be considered in an interpretation of spectral data in solution.

3.3. NMR spectroscopy

Combination of ^{1}H and ^{13}C NMR spectroscopy is a useful tool to detect *E*/*Z* photoisomerization on exocyclic C=C bond and *s-cis*/*s-trans* conformational changes on carboxy ester group of aryl-methylidene-pyrrolinones based on pyrrolinone esters [21,22]. So the same procedure was applied to the Pechmann dyes under study. Nevertheless, in this case no changes of NMR spectra were found even after several weeks of standing on daylight. So we conclude, that *E* isomers of Pechmann dye heteroanalogues do not undergo photoisomerization. Furthermore, they are also highly stable with respect to light induced decomposition, which is in sharp contrast with the behaviour of original Pechmann dye (*exo*-5,5-dilactone), the solution of which decolorizes on exposure to daylight during few hours by our experience.

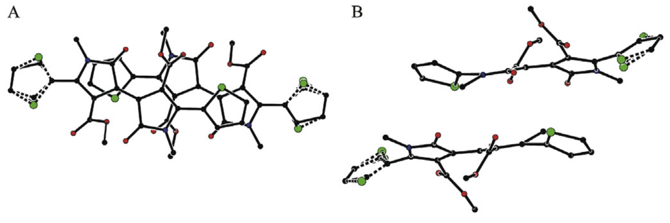


Fig. 2. X-ray structure of π–π stacked dimer of compound **2m** with highlighted conformational disorder on pendant thiophenes (A – perpendicular, B – along a pyrrolinone plane).

Full assignment of NMR chemical shifts is summarized in Table 2 as the numbering of atoms of prepared dyes as shown in Fig. 3. ^{1}H chemical shifts of methyl and methylene protons of carboxy ester group of compounds **1** (**1m**) and **3** (**3m**) do not show considerable differences observed for *s-trans* and *s-cis* arrangement of aryl-methylidene-pyrrolinones [21,22], that may be caused by a remarkable out-of-plane torsion of this side group in all Pechmann dye heteroanalogues, suggestive of relatively free rotation on NMR time scale. Similar lability of pendant thiophenes orientation may explain an absence of distinct signals of *s-trans* and *s-cis* rotamers of compounds **2**–**3m**., i.e., the signals of thiophene localized protons and carbons correspond to an average over both conformers.

3.4. Absorption and fluorescence

Absorption spectra of all prepared compounds were measured in DMSO and 2-MeTHF at room temperature (Table 3). TD DFT computed excitation energies for various conformations of compounds **1**–**3m** including the solvent effect of DMSO by polarized continuum model (PCM) are summarized in Table 4. None of the compounds fluoresce in solution at room temperature, while all of them show fluorescence at low temperature in MTHF solvent glass (Table 3). Solid-state fluorescence of the powders was detected in some cases (**1m**, **4**, **4m**), but never for thiophene substituted derivatives **2**–**3m**.

All compounds show only one strong HOMO–LUMO absorption band in the visible region. The room temperature absorption spectra in both solvents show similar shape and a bathochromic shift of 9–23 nm in more polar DMSO compared with MTHF (Table 3). The vibronic structure is detectable for more planar non-alkylated compounds (Figs. 4 and 5) with the absolute maximum corresponding to 0–1 vibronic transition for **1** and **4** (Fig. 4) and to 0–0 band for relatively more planar thienyl substituted **2** (Figure 5) and **3**. Further deviation from planarity caused by N-alkylation is manifested by more blurred spectra with 0–1 absolute maxima for all compounds and 0–0 vibronic transition observed only as a barely discernible long-wavelength shoulder (Figs. 6 and 7). On the other hand, fluorescence excitation spectra in a low temperature MTHF glass show considerably better resolved vibronic structure with 0–0 transitions detectable as a (usually) absolute maximum in all eight cases, enabling the comparison with theoretical excitation energies. Although the PCM parameters describing the solvent effect of highly polar [32] MTHF glass are not available in Gaussian software package [25], there was recently shown a good correlation between experimental 0–0 vibronic maxima in this glass and theoretical PCM TD DFT excitations energies obtained for DMSO parameterization as a representative of highly polar environment [33]. The theoretical results generally reflect all trends observed experimentally, i.e. bathochromic (and hyperchromic) effect accompanying heterosubstitution (**1**–**3**), marginal effect of the type (methyl- vs. ethyl) of alkyl in ester group in position 3 (**2** vs. **3**) and a bathochromic (but hypochromic) effect of N-alkylation. Quantitatively, the theoretical wavelengths are underestimated by 13 and 19 nm for phenyl derivatives **1** and **1m**, respectively, while an agreement between theory and experiment for thienyl substituted derivatives **2**–**3m** is outstanding: absolute deviation is less than 5 nm for (experimentally detected) **2m** rotamer with *s-cis* ester and *s-trans* thiophene arrangement. A bathochromic and hyperchromic effect of conjugation extension (**1**–**4**) was not treated theoretically, because of considerably higher computational costs for compounds **4** and **4m** in their possible rotamers of 2-naphthyl [20]. Compound **1m** absorbs in MTHF at room temperature at 560 nm, i.e. shows only 2 nm hypsochromic shift with respect to the reported derivative without carboxyesters in the 3.3′-positions, although the planarity of **1m** is more distorted (50° vs. 38° by DFT). We ascribe this effect to a compensation of the non-planarity on single bond (phenyl–pyrrolinone) by a non-planarity on central double bond, causing bathochromic shift through the Brunings–Corvin effect [34], observed e.g. for sterically hindered indigo derivatives [35].

Table 2
^{1}H and ^{13}C chemical shifts NMR for compounds **1**–**4** (A) and for *N*-methylated compounds **1m**–**4m** (B) in DMSO-D$_6$.

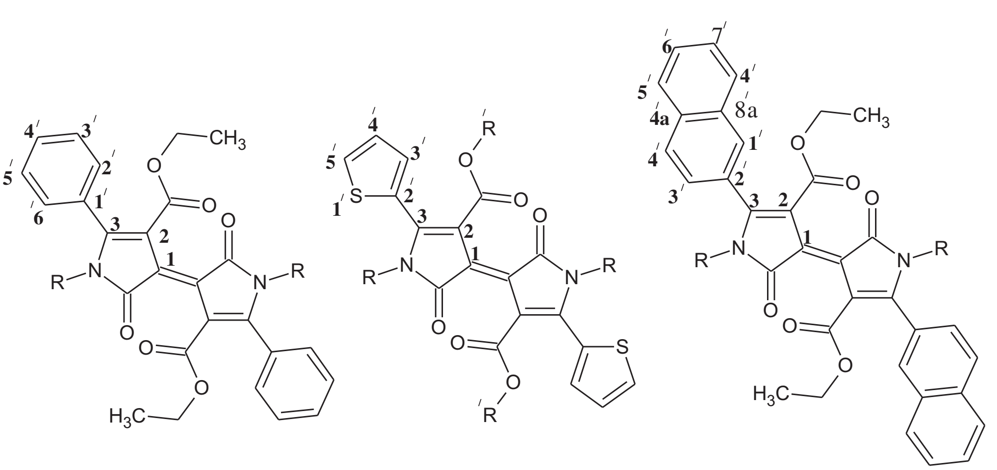
(A) For compounds **1**–**4**

H/C no.	**1**		**2**		**3**		**4**	
	δ(^{1}H)	δ(^{13}C)	δ(^{1}H)	δ(^{13}C)	δ(^{1}H)	δ(^{13}C)	δ(^{1}H)	δ(^{13}C)
(NH)	11.19	–	11.39	–	11.35	–	11.34	–
C=O	–	168.2	–	167.7	–	167.7	–	168.2
1	–	128.3	–	129.9	–	130.0	–	128.3
2	–	108.7	–	107.3	–	107.7	–	109.2
3	–	151.8	–	144.1	–	143.9	–	151.7
COO	–	164.2	–	164.7	–	164.3	–	164.3
CH$_2$	4.16	60.3	–	–	4.23	60.4	4.21	60.3
CH$_3$	1.19	14.0	3.74	51.5	1.27	14.1	1.21	14.0
1′	–	128.7	–	–	–	–	8.38	129.3
2′	7.72	128.8	–	127.5	–	127.4	–	126.1
3′	7.56	128.6	7.98	132.8	7.96	132.6	7.67	125.2
4′	7.59	131.3	7.33	128.3	7.33	128.2	8.08	128.0
4a′	–	–	–	–	–	–	–	133.9
5′	7.56	128.6	8.07	134.8	8.06	134.6	8.04	127.8
6′	7.72	128.8	–	–	–	–	7.72	128.3
7′	–	–	–	–	–	–	7.69	127.9
8′	–	–	–	–	–	–	8.06	128.9
8a′	–	–	–	–	–	–	–	132.1

(B) For *N*-methylated compounds **1m**–**4m**

	1m		**2m**		**3m**		**4m**	
(N–CH$_3$)	2.96	28.1	3.17	28.9	3.15	28.8	3.05	28.3
C=O	–	166.6	–	166.6	–	166.6	–	166.7
1	–	127.3	–	127.7	–	127.9	–	127.4
2	–	109.0	–	109.5	–	110.1	–	109.3
3	–	155.9	–	148.2	–	148.2	–	155.9
COO	–	163.3	–	164.0	–	163.6	–	163.4
CH$_2$	4.03	60.0	–	–	4.13	60.5	4.21	60.0
CH$_3$	1.03	13.9	3.66	51.6	1.16	14.1	1.01	14.0
1′	–	128.3	–	–	–	–	8.27	130.0
2′	[a]	129.4	–	126.6	–	126.6	–	126.0
3′	[a]	128.4	7.74	133.4	7.71	133.2	7.72	126.0
4′	[a]	130.7	7.35	128.1	7.34	128.1	8.13	127.8
4a′	–	–	–	–	–	–	–	133.5
5′	[a]	128.4	8.07	132.6	8.06	132.5	8.08	127.8
6′	[a]	129.4	–	–	–	–	7.70	128.0
7′	–	–	–	–	–	–	7.68	127.1
8′	–	–	–	–	–	–	8.10	128.7
8a′	–	–	–	–	–	–	–	132.1

[a] 7.53–7.71 (10H, m, aromatic protons).



1 - 4 R= H **1m - 4m** R= CH$_3$ ′R= CH$_3$ (2) ′R= C$_2$H$_5$ (3)

Fig. 3. The structures of prepared dyes and numbering of atoms as NMR data in Table 2.

Table 3
Absorption, fluorescence emission (Fl.), excitation (Ex.) spectra and molar absorption coefficients of prepared compounds.

Compound	2-Me–THF			DMSO		Fl. max. solid (nm)
	Abs. max (nm)	Fl. max 77 K (nm)	Ex. max. 77 K (nm)	Abs. max. (nm)	ε (L cm^{-1} mol^{-1})	
1	556, 585	642, 694	568, 613	572, 605	15,700	–
1m	560	653, 698	578, 626	573	13,400	755
2	589, 627	680, 731	608, 654	605, 643	34,300	–
2m	593	693, 746	615, 665	602	27,600	–
3	589, 627	683, 731	617, 663	607, 644	39,100	–
3m	591	689, 741	617, 666	609	31,200	–
4	571, 604 (sh)	656, 707	579, 630	589, 619 (sh)	28,800	705
4m	569	663, 708	579, 634	581	23,800	763

The underlined values are the absolute absorption maxima.

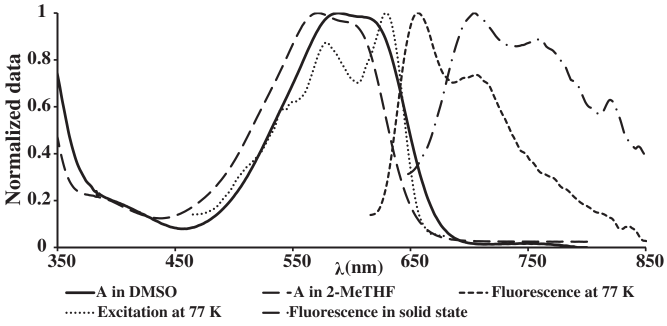


Fig. 4. Absorption and fluorescence spectra of compound **4**.

An absence of fluorescence in solution for all eight compounds is probably based upon considerable extension of the central carbon–carbon bond in the lowest S_1 excited state. The DFT computed length of the central C=C bond of **1m** (1.374 Å) in S_0 agrees quite well with experiment (1.369 Å) giving thus a good chance for the relevance of theoretical modelling based on (TD) DFT. As the excited state geometry optimisations by TD DFT are extremely time consuming, they were carried out only for the model NH analogue of Pechmann dye without the side chain carboxy ester groups. When going from **1m** to **1**, the lengths of the central C=C bond in S_0 state is only slightly lengthened (1.376 Å) by DFT, while the absence of 3,3′substituents makes the model compound planar in central part and, consequently, the C=C bond is shorter (1.372 Å). TD DFT optimisation gives fully planar molecule in the S_1 state, i.e. the central part remains planar, although the central bond is remarkably lengthened (1.410 Å) and phenyl–pyrrolinone dihedral angle is near 180°, as the length of corresponding exocyclic single bond is considerably shortened (from 1.458 Å in S_0 to 1.442 Å in S_1). By our opinion, the relatively weak central bond in excited state can undergo rotations leading to a proximity of S_1 and S_0 hypersurfaces near the excited state equilibrium geometry and consequent internal conversion. An absence of eventual *cis* isomer in solution, confirmed by NMR, means either that rotation in excited state is limited (hindered), or the raised *cis* isomer is thermally highly unstable in the ground state.

Last, but not the least, an absence of solid-state fluorescence in thiophene containing derivatives should be mentioned. The crystal environment can be considered as rigid similarly to the solvent glass that should limit the excited state geometrical relaxation, but also enables various bimolecular specific interactions like energy and electron transfer [36], absent in diluted (frozen) solutions. We will discuss only the difference between compounds **1m** and **2m**, for which the structural interactions in crystal are known from X-ray diffractometry. In the case of compound **1m**, there are no π–π stacking and other strong interactions, thus its solid-state fluorescence can be considered as a result of conserved properties of the individual molecules in the rigid environment [37]. On the other hand, compound **2m** crystallizes as π–π stacked dimer, which in fact may not automatically mean the absence of fluorescence [38]. We carried out single point energy calculation of the dimer of **2m** at DFT B3LYP/6-311G(d,p) level on experimental geometry (Fig. 2) and evaluated HOMO and LUMO splitting-in-dimer as these energy splittings in the case of a centrosymmetrical dimers relate to electron transfer integrals and, consequently, to the probability of electron-transfer inside the dimer [39]. We found HOMO splitting of 107 meV and LUMO splitting 80 meV, i.e., the values are sufficiently high to enable the transfer in both splitted orbitals after excitation. The formation of radical cation/radical anion pair is thus possible in a dimer of **2m** and its subsequent recombination may form the main fluorescence quenching channel in crystal.

Table 4
PCM (DMSO) TD DFT excitation energies recomputed to wavelengths (λ_{00}) and oscillator strengths (f_{osc}) of the longest wavelength HOMO–LUMO absorption band. The data for more probable ester conformation are bolded.

Compound	Ester conformation	Thiophene conformation	λ_{00} [nm]	f_{osc}
1	trans	–	**600**	**0.658**
	cis	–	603	0.613
1m	trans	–	**607**	**0.453**
	cis	–	599	0.384
2	trans	trans	647	0.774
		cis	640	0.816
	cis	trans	**658**	**0.748**
		cis	**657**	**0.735**
2m	trans	trans	653	0.612
		cis	648	0.607
	cis	trans	**669**	**0.616**
		cis	**659**	**0.601**
3	trans	trans	648	0.778
		cis	642	0.804
	cis	trans	**659**	**0.733**
		cis	**658**	**0.719**
3m	trans	trans	654	0.609
		cis	649	0.597
	cis	trans	**670**	**0.603**
		cis	**660**	**0.587**

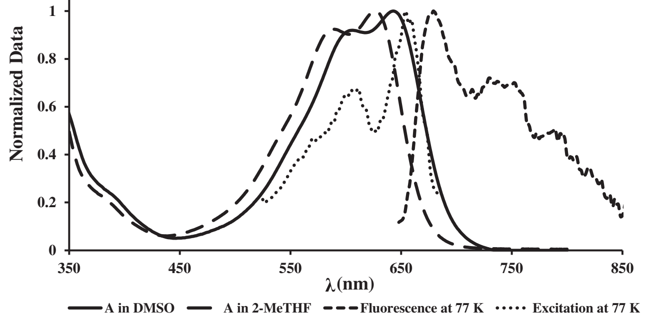


Fig. 5. Absorption and fluorescence spectra of compound **2**.

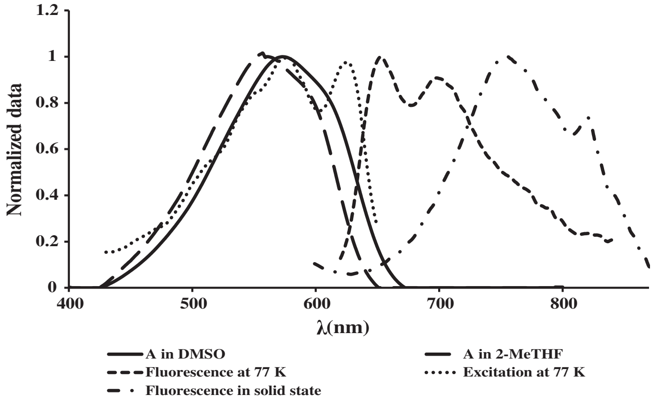


Fig. 6. Absorption and fluorescence spectra of compound **1m**.

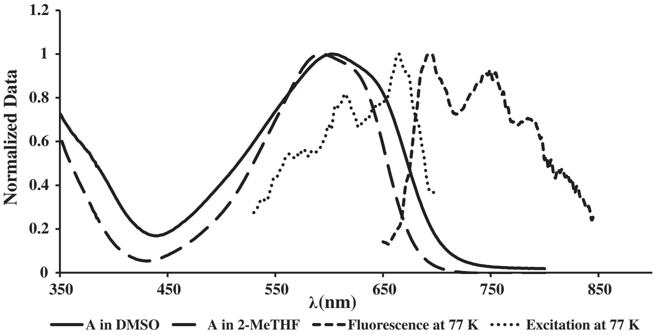


Fig. 7. Absorption and fluorescence spectra of compound **2m**.

4. Conclusion

Eight highly photo-stable Pechmann dye *N*-analogues were synthesized. They were found as *E*-isomers, i.e. all-*trans* 1,6-(hetero)aryl-1,3,5-hexatrienes cyclized into two lactam rings. Both thiophene to phenyl heterosubstitution and conjugation extension caused a bathochromic shift. Only low temperature fluorescence in solvent glass was observed for all derivatives. The thiophene derivatives show no solid-state fluorescence, a feature that was ascribed to excited state electron transfer inside a π–π stacked dimer and a consequent recombination of radical cation/radical anion pair. (TD) DFT computations were able to reliably describe all observed structural and spectral phenomena.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.04.010.

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