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2	stilbene and pyrazoline based chromophores
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26 Abstract

27 In this work we present the synthesis, spectroscopic and nonlinear optical properties of *pushpull* type organic dyes based on 1-phenyl-2-pyrazoline or 4-(dimethylamino)phenyl 28 29 chromophores as a donor part, and bridged by a double bound ortho- or meta- substituted 30 nitrophenyl group as an acceptor. For the optical measurements we have used the poly(methyl 31 methacrylate) based thin films doped with the dyes. Third harmonic generation measurements 32 were performed under the picosecond laser regime with excitation wavelength at 1064 nm. 33 The experimental results confirmed that investigated systems can be used as the efficient 34 nonlinear optical systems for harmonic of light generation (tripled but also doubled frequency). It has also been proved the strong dependence between chemical structure 35 36 (position of electron-acceptor moiety as well as the type of electron-donor unit) and nonlinear 37 optical (NLO) response coming from series of isomers and derivatives.

38 Keywords: organic dyes, push-pull molecules, nonlinear optics, pyrazoline, Horner–
39 Wadsworth–Emmons (HWE) reaction

40

41 **1. Introduction**

Nowadays a number of research groups put a great effort into their work to achieve 42 new organic materials with desired properties and better parameters, as well as develop new 43 44 solutions to be implemented in certain applications, such as sensors, photovoltaics, 45 electroluminescent diodes, lasers, switchers and others [1-4]. One of the very promising, and still not enough investigated, group of organic dyes for photonic purposes is pyrazolines. The 46 47 and properties of 3-(2,2-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole synthesis 48 (DCNP), was patented by Gordon and Bothwell [5] and in the same year published for the 49 first time by group of Allen [6]. The compound became a very attractive organic photonic 50 material due to its great nonlinear optical (NLO) and electro-optic response. A lot of further

51 studies concerning NLO [7, 8] as well as light amplification properties of DCNP were done 52 by Miniewicz group, emphasizing the unique features of the compound [9-11]. It has also become reasonable to search for new analogues of the dye, that may be interesting from both, 53 54 a scientific, as well as an application point of view. Therefore, we have designed, synthesized and characterized some derivatives of DCNP, based on 1-phenyl-2-pyrazoline electron-donor 55 56 part and various electron-withdrawing moieties conjugated by a double bond. Basing on 57 chosen compounds from the dyes family we have shown their high potential in NLO purposes 58 (second harmonic generation (SHG), third harmonic generation (THG)) [12, 16, 17], in light amplification (amplified spontaneous emission (ASE), random lasing (RL)) [13] or in optical 59 switching (measurements of completely reversible photoinduced birefringence) [14, 15]. 60

61 In this paper we show the synthetic route for two new derivatives of 1-phenyl-2pyrazoline, π -conjugated with ortho- or meta- substituted nitrophenyl group as an electron 62 acceptor, and characterize their 3rd order NLO response (THG), as well as basic spectroscopic 63 properties. In order to emphasize the role of the heterocyclic fragment in observed NLO 64 65 behavior, we compare the dyes with similar in the electron acceptor part stilbene derivatives, where 1-phenyl-2-pyrazoline was substituted by para-(dimethylamino)phenyl donor group. 66 Obtained results show significant influence of the electron donor part on measured 3rd order 67 nonlinear susceptibilities. Moreover, taking into consideration also the earlier described third 68 69 pyrazoline isomer (para-nitrophenyl derivative [16]), we can find a correlation between 70 chemical structure (position of the electron-acceptor moiety as well as the type of electron-71 donor unit) and NLO response coming from series of isomers and derivatives, what can be 72 useful in molecular design of chromophores with desired properties. The chemical structures 73 of the synthesized compounds are shown in Fig. 1.



Figure 1. Synthetic route for the new *push-pull* type pyrazoline dyes and their stilbenecounterparts.

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79 **2. Experimental section**

General information and technical details concerning the synthetic route characterization
(Chapter S1) as well as samples preparation methodology (S2), computational details (S3) and
description of the SHG experimental set-up (S4) are presented in Supplementary Information
(SI).

84

85 **2.1. Synthesis**

86 Synthesis of the 1-phenyl-2-pyrazoline-3-carboxyaldehyde:

87 This compound was prepared with 37-52 % yield, according to the literature procedure

- 88 [8, 14]. ¹H NMR (300 MHz, CDCl₃): δ 3.12 (t, 2H, CH₂, J=11.6 Hz), 4.08 (t, 2H, CH₂, J=11.6
- 89 Hz), 7.05 (tt, 1H, p-ArH, J=7.3 Hz, J=1.1 Hz), 7.21 (m, 2H, o-ArH), 7.36 (m, 2H, m-ArH);

¹³C NMR (75 MHz, CDCl₃): δ 27.41 (CH₂), 49.53 (NCH₂), 114.34, 122.49, 129.44, 142.45,
149.38, 185.80 (CHO).

92

93 Synthesis of diethyl 2-nitrobenzylphosphonate and diethyl 3-nitrobenzylphosphonate:

A mixture of 2- or 3-nitrobenzyl bromide (5.3 g, 0.025 mol) and triethyl phosphite 94 (16.6 g, 0.10 mol) was stirred and heated at about 150-160 °C (oil bath temperature) for 1 95 hour with continuous distillation of the ethyl bromide produced. The reaction mixture was 96 cooled to room temperature and evaporated to dryness (20 mmHg, boiling water bath). 97 98 Obtained residue was dissolved in ethyl acetate (100 ml) and washed with saturated solution 99 of NaHCO₃ (6x30 ml). The organic phase was dried over anhydrate Na₂SO₄ and concentrated 100 in vacuum. Obtained thick oily residue was washed with petroleum ether (5x20 ml) and the 101 finally dried in vacuum (~5 mmHg) yielding diethyl 2-nitrobenzylphosphonate (5.4 g, 79 %) 102 and diethyl 3-nitrobenzylphosphonate (5.6 g, 82 %) as yellow oils. After confirmation of its structure by ¹H and ³¹P NMR spectroscopy, both compounds were used in the next step 103 without further purification. NMR spectra of crude diethyl 2-nitrobenzylphosphonate [19, 20] 104 and diethyl 3-nitrobenzylphosphonate [21, 22] were in accordance with literature data. 105

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107 Synthesis of AM-oNO₂, AM-mNO₂ stilbenes and PY-oNO₂, PY-mNO₂ pyrazolines:

To a cooled (water-ice bath) solution of crude diethyl 2-nitrobenzylphosphonate or diethyl 3-nitrobenzylphosphonate (2.7 g, 10 mmol) and appropriate aldehyde (10 mmol) in a mixture of anh. DMF (20 ml) and anh. EtOH (20 ml) a solution of EtONa (15 mmol) in ethanol was added dropwise over 30 minutes. Obtained reaction mixture was stirred upon cooling for 1 hour and next left standing overnight at room temperature. Afterward, a reaction mixture was poured into a cold water (200 ml) and stirred for 30 minutes.

In the case of stilbenes, **AM-oNO**₂ and **AM-mNO**₂, the aqueous phases were extracted with dichloromethane (1x50, 3x20 ml) and dried over anh. Na₂SO₄. The solvent was evaporated and obtained crude products were purified as indicated. Crude **AM-oNO**₂ was purified using short-column chromatography (silica gel, AcOEt) and further recrystallized from diethyl ether, while **AM-mNO**₂ was purified using column chromatography (silicagel, petroleum ether/AcOEt, 2:1, V/V) and further recrystallized from dichloromethane/petroleum ether mixture.

In the case of pyrazolines, **PY-oNO₂** and **PY-mNO₂**, the precipitated solids were filtered off, washed with water (5x20 ml) and dried on air to give the crude products which were further purified using column chromatography (silica gel, petroleum ether/AcOEt, 2:3, V/V) and then recrystallized from diethyl ether.

(E)-2⁻-nitro-4-dimethylaminostilben (AM-oNO₂): yield 20 %; dark red powder; m.p. 86-87 125 °C (lit. m.p. 87-89°C [19]); ¹H NMR (600 MHz, CDCl₃): δ 3.03 (s, 6H, 2xCH₃), 6.74 (d, 2H, 126 127 J=7.8 Hz, m-ArH (C₆H₄NMe₂)), 7.09 (d, 1H, J=16.2 Hz, =CH), 7.33 (t, 1H, J=7.8 Hz, 4-ArH), 7.44 (d, 1H, J=16.2 Hz, =CH), 7.46 (d, 2H, J=7.8 Hz, o-ArH (C₆H₄NMe₂)), 7.56 (t, 1H, 128 J=7.2 Hz, 5-ArH), 7.79 (d, 1H, J=7.8 Hz, 6-ArH), 7.92 (d, 1H, J=7.8 Hz, 3-ArH); ¹³C{¹H} 129 NMR (150 MHz, CDCl₃): δ 40.35, 112.24, 118.32, 124.77, 126.82, 127.50, 128.42, 132.82, 130 133.77, 134.30, 147.71, 150.76 (signal of the one quaternary carbon missing due to 131 132 coalescence and overlaps); HRMS: calcd for $C_{16}H_{17}N_2O_2$ (M+H)⁺ 269.1290, found 269.1277. (E)-3'-nitro-4-dimethylaminostilben (AM-mNO₂): yield 25 %; orange powder; m.p. 146-133 148 °C (lit. m.p. 148 °C [20, 21]); ¹H NMR (600 MHz, CDCl₃): δ 3.04 (s, 6H, Me₂N), 6.75 (d, 134 2H, J=7.7 Hz, m-ArH (C₆H₄NMe₂)), 6.94 (d, 1H, J=16.2 Hz, =CH), 7.18 (d, 1H, J=16.2 Hz, 135 136 =CH), 7.46 (d, 2H, J=7.7 Hz, o-ArH (C₆H₄NMe₂)), 7.49 (t, 1H, J=7.7 Hz, 5-ArH), 7.76 (d, 1H, J=7.7 Hz, 6-ArH), 8.04 (d, 1H, J=8.1 Hz, 4-ArH), 8.33 (s, 1H, 2-ArH) (¹H NMR data are 137 in agreement with those reported in the literature [24]); ${}^{13}C{}^{1}H{}$ NMR (150 MHz, CDCl₃): 138

139 δ 40.36, 112.30, 120.30, 120.96, 121.48, 124.47, 128.08, 129.39, 131.70, 131.88, 140.15,

140 148.76, 150.64; HRMS: calcd for $C_{16}H_{17}N_2O_2 (M+H)^+$ 269.1290, found 269.1281.

(E)-3-(2-nitrostyryl)-1-phenyl-2-pyrazoline (PY-oNO₂): yield 45 %; dark red powder; m.p. 141 158-159 °C; ¹H NMR (600 MHz, CDCl₃): δ 3.20 (t, 2H, J=10.8 Hz, CH₂), 3.96 (t, 2H, J=10.8 142 Hz, CH₂), 6.92 (tt, 1H, J=0.6 Hz, J=7.2 Hz, p-PhH), 7.12 (dd, 2H, J=0.6 Hz, J=8.4 Hz, o-143 PhH), 7.15 (d, 1H, J=16.2 Hz, =CH), 7.26 (d, 1H, J=16.2 Hz, =CH), 7.33 (m, 2H, m-PhH), 144 7.42 (dt, 1H, J=1.2 Hz, J=7.8 Hz, 4-ArH), 7.62 (dt, 1H, J=1.2 Hz, J=7.8 Hz, 5-ArH), 7.78 145 (dd, 1H, J=1.2 Hz, J=8.4 Hz, 6-ArH), 7.98 (dd, 1H, J=1.2 Hz, J=8.4 Hz, 3-ArH); ¹³C{¹H} 146 NMR (150 MHz, CDCl₃): δ 30.43, 48.17, 113.04, 119.81, 124.98, 125.96, 126.84, 127.70, 147 128.06, 129.23, 132.34, 133.15, 144.56, 147.72, 149.81; HRMS: calcd for C₁₇H₁₆N₃O₂ 148 149 (M+H)⁺ 294.1242, found 294.1245.

(E)-3-(3-nitrostyryl)-1-phenyl-2-pyrazoline (PY-mNO₂): yield 56 %; light brown powder; 150 m.p. 181-183 °C; ¹H NMR (600 MHz, CDCl₃): δ 3.17 (t, 2H, J=10.2 Hz, CH₂), 3.94 (t, 2H, 151 J=10.2 Hz, CH₂), 6.62 (d, 1H, J=16.2 Hz, =CH), 6.91 (t, 1H, p-PhH), 7.10 (d, 2H, o-PhH) 152 7.28-7.35 (m, 3H, m-PhH+ =CH), 7.53 (t, 1H, J=7.8 Hz, 5-ArH), 7.78 (d, 1H, J=7.8 Hz, 6-153 ArH), 8.10 (d, 1H, J=7.8 Hz, 4-ArH), 8.31 (s, 1H, 2-ArH); ¹³C{¹H} NMR (150 MHz, CDCl₃): 154 δ 30.38, 48.12, 113.00, 119.05, 119.80, 122.17, 124.76, 128.98, 129.24, 129.68, 131.76, 155 138.72, 144.58, 148.79, 149.27; HRMS: calcd for C₁₇H₁₆N₃O₂ (M+H)⁺ 294.1242, found 156 294.1243. 157

158

159 2.2. Spectroscopic and optical measurements

Basic linear optical properties of the fabricated materials, i.e. absorption and emission spectra, were measured using the Jasco V-670 spectrophotometer and Hitachi FL-4500 spectrofluorometer. Emission spectra from the layers were gathered by the excitation of samples at their absorption maxima.

167 For the screening and interpretation of results of both, SHG (more details in SI materials - S4 chapter) and THG measurements, different theoretical and experimental 168 169 approaches were utilized. Third harmonic generation phenomenon serves for the characterization of 3rd order nonlinear optical parameter - susceptibility $\chi^{(3)}$. In the process of 170 THG, frequency ω of initial beam is converted to 3ω in the output. The main difference 171 172 between material restrictions for SHG and THG is that for the latter one the symmetry of studied nonlinear optical medium does not have any demands. The Kubodera and Kobayashi 173 174 model was used for the analysis of THG in the materials (1) [26-29]:

175
$$\chi^{(3)} = \frac{2}{\pi} \chi_s^{(3)} L_c^s \frac{\alpha/2}{1 - exp(-\alpha l/2)} \sqrt{\frac{I_{3\omega}}{I_{3\omega}^s}}$$
(1)

where the L_c^s represents coherence length of silica (reference material for THG investigations), *l* is sample thickness, α - linear absorption coefficient and $I_{3\omega}^s$, $I_{3\omega}$ are the THG intensity for the reference and investigated materials, respectively. In our case the thin silica glass plate has been used as the reference material ($\chi_s^{(3)} = 2.0 \times 10^{-2} m^2 \cdot V^{-2}$).

180

181 **3. Results and discussion**

182 **3.1. Synthesis**

183 Synthetic route for all final dyes was shown in Fig. 1. Examined compounds were via 184 prepared the Horner-Wadsworth-Emmons (HWE) reaction of 4dimethylaminobenzaldehyde (in the case of AM-oNO₂ and AM-mNO₂) or 1-phenyl-2-185 pyrazoline-3-carboxyaldehyde (in the case of PY-oNO₂ and PY-mNO₂) with 2- or 3-186 nitrobenzylphosphonates in a mixture of anhydrous ethanol and anhydrous DMF (1:1, V/V) in 187 the presence of 1.5 equivalent of sodium ethoxide as a base. Starting 2- and 3-188

nitrobenzylphosphonates were synthesized by the classical *Arbuzov* reaction of commercial 2and 3-nitrobenzyl bromides and excess of the triethylphosphite at 150-160 °C. After confirmation of the structures by ³¹P and ¹H NMR, the crude phosphonates were used in HWE reaction without further purification. The 1-phenyl-2-pyrazoline-3-carboxyaldehyde used as substrate for the synthesis of PY-oNO₂ and PY-mNO₂ was prepared in reaction of 1phenyl-2-pyrazoline [12, 18] and the *Vilsmeier-Haack* reagent [30] using literature procedure [12, 31].

Using sodium ethoxide as a base and DMF-EtOH mixture as a solvent allowed us to obtain all final products selectively as (E)-isomers. Such result is in the agreement with literature data [32]. Structures of all final dyes were confirmed by ¹H and ¹³C NMR, and high resolution mass spectrometry (HRMS). Stereochemistry of the compounds double bond was determined on the basis of the value of the coupling constant of the vinylic protons (³*J*) in ¹H NMR spectra.

Stilbenes AM-oNO₂ and AM-mNO₂ are known in the literature. In case of stilbene AM-oNO₂, its photochemical behavior was investigated [23]. Derivative AM-mNO₂ was described by Güsten and Salzwedel, who investigated NMR spectra of a series of substituted stilbenes [24], while Syz and Zollinger analyzed its photoisomerization behavior [25].

206

207 **3.2. Theoretical studies**

All four compounds exist as a mixture of 3 conformers: two – *trans* and one – *cis*. The optimized geometries of all investigated isomers are presented in Fig. 2. For pyrazoline derivatives *trans 1* isomers are the lowest in energy. The second *trans* isomers are 3.98 and 3.28 kcal/mol higher in energy and their contribution to population according to *Boltzmann* distribution in the room temperature equals to 14 and 20 % for PY-oNO₂ and PY-mNO₂, respectively. *Cis* isomers are less stable - 5.79 and 6.60 kcal/mol higher in energy, and their

abundance is 4 % and 6 % for PY-oNO₂ and PY-mNO₂, respectively. For stilbene derivatives both optimized *trans* isomers are almost equal in energy (difference of 0.01 and 0.15 kcal/mol between *trans 1* and *trans 2* conformers for AM-oNO₂ and AM-mNO₂, respectively). Their abundances are comparable and they are 46 % and 47 % for AM-oNO₂ *trans 1* and *trans 2* and 41 % and 54 % for AM-mNO₂ *trans 1* and *trans 2*. The *cis* isomers are higher in energy (4.46 and 5.22 kcal/mol for AM-oNO₂ and AM-mNO₂) and their contribution to population is equal to 7 % and 5 %, respectively.





Figure 2. Optimized molecular structures of PY-oNO₂, PY-mNO₂, AM-oNO₂ and AM-mNO₂
conformers. DFT/B3LYP/6-311++G(d,p). Atom colors labeling: C – dark gray, H – light
gray, S- yellow, N – blue, O - red.

225

3.3. Spectroscopic and nonlinear optical properties

- 227 Normalized linear UV-Vis absorption and emission spectra from studied layers were
- shown in Fig. 3. It is visible that the absorption spectra of each sample exhibits a multiband
- structure, what is more pronounced for *ortho* isomers.



230

Figure 3. Absorption and emission experimental and separated simulated spectra for allopitimized isomers of the investigated systems.

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In order to interpret the obtained spectra vertical excitations at CAM-B3LYP/6-311++G(d,p) level of theory were calculated. As one can see the position of transitions in experimental and simulated spectra fit satisfactory, although the calculations underestimate the intensity of shorter wavelength transitions in *ortho* substituted compounds. The multiband structure of these spectra is connected with two transitions. The first one (363 nm in PY-oNO₂ and 350 nm in AM-oNO₂) can be assigned to HOMO \rightarrow LUMO +1 and the second one (425 and 419

nm, respectively) to HOMO \rightarrow LUMO transitions. Selected orbitals for the most stable isomers obtained at B3LYP/6-311+G(d,p) level of theory are presented in Fig. 4. These two transitions for *ortho* isomers are predicted to be separated by ca. 90 nm. For *meta* isomers H \rightarrow L+1 is significantly blue-shifted and both peaks are expected to be separated by only ca. 30-40 nm. According to the FWHM (full width at half maximum), which is above 50 nm, they are overlapped. Moreover, the additional splitting of the lines can be connected with the abundance of all conformers in the experimental sample.

CHR MA



- 311++G(d,p) level of theory).

- **Table 1.** λ_{calc} calculated at CAM-B3LYP/6-311++G(d,p) level of theory (THF solution) with
- assignment of low electronic singlet excitations of PY-oNO₂, PY-mNO₂, AM-oNO₂ and AM-
- 254 mNO₂ investigated isomers

Investigated		ΔE^{H-L}	λ^{calc}		
molecules		[eV]	[nm]	f	Assignment ^a
	trans		427.8	0.818	$H \rightarrow L(84\%) + H - 1 \rightarrow L(6\%) + H - 1 \rightarrow L + 1(8\%)$
	1	4.76	345.5	0.486	$H\rightarrow L+1(82\%) + H\rightarrow L(6\%)$
	trans		432.7	0.486	$H \rightarrow L(80\%) + H \rightarrow L + 1(12\%)$
PY-	2	4.79	356.5	0.593	$H \rightarrow L+1(79\%) + H \rightarrow L(12\%)$
oNO ₂					$H \rightarrow L(86\%) + H \rightarrow L + 1(6\%)$
		4.00	409.9	0.475	H→ L +1(63%) + H -7→ L (12%)
	CIS	4.86	323.7	0.461	$H_7 \rightarrow I(35\%) + H_7 \rightarrow I(9\%) + H_7$
			311.0	0.107	11-7 $7L(3370) + 11-4$ $7L(370) + 11-4$
					$3 \rightarrow L(13\%) + H \rightarrow L + I(19\%)$
					$H \rightarrow L(63\%) + H \rightarrow L + 1(28\%) + H - 1 \rightarrow L(6\%)$
			399.2	0.721	H→ L +1(65%) + H → L (23%) + H -1→ L (6%)
	trans	4 7 1	361.4	0.714	
	1	4.71	272.0	0 1 1 1	$H \rightarrow L+6(72\%)$
	1		262.0	0.173	$H-3 \rightarrow L(63\%) + H-4 \rightarrow L(10\%) + H-$
PY-					$1 \rightarrow L(10\%)$
mNO ₂			415.0	0.725	$H \rightarrow L(49\%) + H \rightarrow L + 1(44\%)$
	trans	4.69	369.6	0.223	$H \rightarrow L+1(49\%) + H \rightarrow L(39\%) + H-1 \rightarrow L(5\%)$
			273.0	0.101	H→L+5(69%)
			369.1	0.262	$H \rightarrow L(75\%) + H \rightarrow L + 1(15\%)$
	cis	4.86	350.1	0.838	$H \rightarrow L+1(77\%) + H \rightarrow L(15\%)$

	trans		415.6	0.727	$H \rightarrow L(86\%) + H - 1 \rightarrow L(9\%)$	
	1	4.91	328.8	0.483	H→L+1(86%)	
	trans	4.91	416.1	0.725	$H \rightarrow L(86\%) + H - 1 \rightarrow L(9\%)$	
AM-	2		329.4	0.489	H→L+1(86%)	
oNOa					$H \rightarrow L(86\%) + H - 1 \rightarrow L(8\%)$	
01102			402.2	0.280	H→L+1(77%)	
	cis	4.98	300.7	0269	$H \rightarrow L+3(20\%) + H-7 \rightarrow L(15\%) +$	
			277.2	0.149	$H \rightarrow L+12(12\%) + H-1 \rightarrow L(9\%) + H-$	
					3→L(7%)	
					H→L+1(92%)	
	trans 1	4.81	351.9	1.278	$H \rightarrow L + 2(42\%) + H - 3 \rightarrow L(30\%)$	
			260.5	0.120	$H \times I + 2(410/2) + H \times 2 \times I (270/2) + H$	
			259.8	0.144	$H \rightarrow L + 2(41\%) + H - 3 \rightarrow L(37\%) + H - H - 3 \rightarrow L(37\%) + $	
					2→L(6%)	
AM-					$H \rightarrow L(82\%) + H - 1 \rightarrow L(11\%)$	
mNO ₂			395.2	0.224	H→L+2(88%)	
	trans	4.78	339.0	1.136	$H \rightarrow L + 6(42\%) + H \rightarrow L + 4(39\%) + H$ -	
	2		281.8	0.104		
			262.4	0.208	$1 \rightarrow L+1(7\%)$	
					$\text{H-3} \rightarrow \text{L}(63\%) + \text{H-2} \rightarrow \text{L}(17\%)$	
	cis	4.90	321.3	0.719	H→L+2(86%)	
^a Labels: H	^a Labels: H – HOMO, L – LUMO. The contribution or transitions > 5 % are included.					

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Calculated parameters presented in Tab. 1 allowed us to assign experimentally observed absorption lines. Maxima observed at 363 and 350 nm for PY-oNO₂ and AM-oNO₂, respectively, can be assigned as $H \rightarrow L+1$. Lines appeared at 425 and 419 nm for these

259 compounds are due to $H \rightarrow L$. In case of *meta* isomers PY-mNO₂ and AM-mNO₂ both $H \rightarrow L$ 260 and $H \rightarrow L+1$ transitions have contribution to observed absorption maxima. In examined group of compounds it is shown that change of $-NO_2$ group position from *meta* to ortho 261 exhibits shift of $H \rightarrow L$ absorption into visible light. 262 Simulated orbitals presented in Fig. 4 confirm also that both $H \rightarrow L$ and $H \rightarrow L+1$ 263

transitions have the *push-pull* character. The electron density transfer occurs from donor 264 stilbene group via -CH=CH- connector onto $C_6H_4NO_2$ acceptor. The character of transition 265 266 does not depend on $-NO_2$ position.

The performed calculations showed that in the $-oNO_2$ compounds the lowest transition 267 is predominantly from HOMO to LUMO, where the electron is mainly localized in the 268 269 nitrophenyl moiety in LUMO. By contrast, in $-mNO_2$ compounds the lowest transition has 270 larger involvement of LUMO+1, in which the electron is delocalized cross the entire 271 molecule. This is consistent with the observation that the *ortho*- substituted nitrophenyl group possesses stronger electron withdrawing ability than meta- substituted ones. Therefore, the 272 273 intramolecular charge transfer character in $-oNO_2$ compounds is more significant and consequently it red shifts the absorption band. 274

275 Afterwards, the fluorescence spectra of the THF solutions doped by the luminescent 276 dyes have been acquired with the use of spectrofluorometer Hitachi F-4500. Two investigated in this paper pyrazoline derivatives emit the light in the range of 450 - 650 nm, but absorption 277 278 maxima of PY-mNO₂ and PY-oNO₂ are localized at 395 and 363 nm, respectively. The latter 279 system possesses also the second but much weaker absorption band localized at 425 nm, 280 which is partially inscribed in the main range of emission for this compound. Molecule PY-281 pNO_2 (which is a constitutional isomer of the abovementioned ones, investigated by us 282 recently [15]) characterizes the highest Stokes shift among presented compounds, which is 283 167 nm. This system possesses also the emission band shifted strongly toward the red range.

In the group of investigated *push-pull* type of low molecular weight systems doped to the PMMA the THG phenomenon has been characterized. Table 2. contains all NLO determined parameters of studied materials. Table S1. (Chapter S5 in SI materials) contains also $\chi^{(2)}$ parameters defined for both laser polarization configurations (*s* and *p*) for the investigated polymeric systems.

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Table 2. Nonlinear optical parameters (3rd order NLO susceptibilities) for the investigated
 polymeric systems.

Compound	$\chi^{(3)} \left[m^2 / V^2 ight]^{ m a, b}$
PY-pNO ₂	8.1 × 10 ^{-21 c}
PY-mNO ₂	1.1×10^{-22}
PY-oNO ₂	4.0×10^{-22}
AM-mNO ₂	5.6×10^{-23}
AM-oNO ₂	3.7×10^{-23}
silica	2.00×10^{-22}

^a – Maker fringes set-up employing the fundamental exit (1064 nm) of a 30 ps Nd:YVO₄ laser
 with a repetition rate of 10 Hz at 532 nm; the energy per pulse was 40 mJ

^b – calculated according to the *Kubodera and Kobayashi* model (taking into account the linear

absorption coefficient)

296 $^{\rm c}$ – literature data [16]

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The third harmonic generation phenomenon has been characterized by the comparable method, where the Maker fringe patterns were measured as a function of incidence angle using a rotational stage and picosecond pulsed laser as the incident beam. The THG results are associated with properties of the each one molecule. As the reference material a thin silica

302 glass plate was used. The characteristic incident angle dependences coming from this 303 measurements are shown in Fig. 5. What is clearly visible, both of the investigated stilbenes present similar NLO answer as the used reference. However, two of the studied pyrazoline 304 derivatives exhibit several times larger THG signal than silica. It seems that electron donor 305 part in the shape of aromatic ring linked to the pyrazoline one is more effective than 3rd order 306 307 amine group used in stilbenes. Furthermore, in one case - not included experimentally in this paper (PY-pNO₂) [17], $\chi^{(3)}$ parameter is even one order of magnitude larger than for the 308 reference material (Tab. 2). Anyway, among the group of pyrazoline derivatives, the ortho 309 isomer can induce four times higher signal than the *meta* one. It can be strictly involved with 310 311 the activation (ortho and para) and deactivation (meta) process (understood as the internal 312 electron transfer) into the aromatic ring (located in the electron acceptor part in the molecule) by proper substituent position. Moreover, presented in this paper two isomers of pyrazoline 313 derivatives in the meaning of the $\chi^{(3)}$ NLO parameter correspond with other representatives 314 from this family of compounds described in literature [16]. Namely, another nonlinear dyes 315 316 containing pyrazoline ring and as the electron-acceptor moiety double nitrile groups (in various structural configuration) characterize the same order of magnitude value of the 3rd 317 318 order nonlinear optical susceptibility. It means that initial hypothesis presenting pyrazoline 319 derivatives group of compounds as the efficient NLO chromophores (SHG/THG converters) was correct [16, 17]. 320



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Figure 5. The typical Maker fringe patterns obtained in THG measurements acquired for: silica glass plate (top) and polymeric systems doped with isomers of pyrazoline derivatives (middle) and two isomers of the stilbene dye (bottom). The experimental results for investigated samples and reference material were collected for the *s* polarization of incident beam.

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Therefore, the concentration influence on the THG signal only for the two most effective representatives on THG phenomenon among investigated materials - pyrazoline derivatives, has been investigated (Fig. 6.). In these cases there is a precise value of the dye concentration above which the increase of NLO answer is observed. In the range of 1.50 % (PY-mNO₂) to 2.25 % (PY-oNO₂) of the dry dye content (w/w) it is observed the threshold which indicates the quantity of the nonlinear medium is going to be more efficient according to the linear growth function. For each compound this dependence is different.



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Figure 6. The measured dye concentration dependence on the 3^{rd} order nonlinear optical susceptibility for PY-mNO₂ (up) and PY-oNO₂ (down) for *s* polarization of incident light.

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By presenting this results we would like to point out that defined values of $\chi^{(3)}$ were determined for the films with 3 % dye content and it can be improved by process optimization due to the used polymer, dye concentration and the used solvent as well. Moreover, the crystallization or aggregation process can be responsible for this particular behavior. By creating more condense matter in the volume of the polymeric film it is possible to gain some optical effects, in this case - NLO response.

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348 4. Conclusions

349 The represents of *push-pull* type of organic molecules based on the 4-350 dimethylaminophenyl group and 1-phenyl-2-pyrazoline moiety have been introduced, both 351 the synthesis method and basic spectroscopic characterization. The THG results obtained 352 from picosecond pulsed laser system have been acquired and analyzed in comparison with the 353 theoretical models. Among the investigated compounds the pairs of derivatives and isomers 354 can be distinguished. They characterize different electron-donor units and spectroscopic features (especially NLO ones) likewise. The experimental results confirmed that investigated 355 systems can be used as the efficient nonlinear optical systems for harmonic of light generation 356 357 (tripled but also doubled frequency). It has been also proved the strong dependence between chemical structure (position of electron-acceptor moiety as well as the type of electron-donor 358 359 unit) and NLO response coming from series of isomers and derivatives. This correlation 360 directly indicates the field where the chemists and physicists can co-operate efficiently. By 361 simple combination of the chemists knowledge and experience in the field of synthesis with 362 the physicists expectations involved with the new, more useful and hybrid or composite 363 materials and their valuable properties can give as the result new device or design unfamiliar 364 solution for various processes. Also in this paper we showed that there is a particular amount

of nonlinear dye concentration in polymeric film (threshold value), which causes sudden 365 366 increase of NLO response due to the THG, even if the active medium absorbs the light in the range of generated harmonics of light. Accordingly, this part of the results can improve 367 368 material's engineering as the very useful and meaningful tool in design new, more effective materials for various applications. It also confirms that individual approach for the 369 370 optimization of already existing systems is needed and should be always done. Presented 371 experimental results indicate that the group of pyrazoline and stilbene derivatives have a great 372 potential in future photonic applications.

373

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382 Supplementary content

Supplementary data with copy of ¹H and ¹³C NMR spectra of examined compounds (AMoNO₂, AM-mNO₂, PY-oNO₂ and PY-mNO₂) can be found, in the online version.

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Highlights:

- Pairs of pyrazoline and stilbene derivatives have been analyzed
- Horner–Wadsworth–Emmons (HWE) reaction was implemented
- Second and third order of nonlinear optical properties were investigated
- Dependence between chemical structure and NLO response was shown