



# Synthesis and nonlinear optical properties of *push-pull* type stilbene and pyrazoline based chromophores



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## ABSTRACT

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

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## 1. Introduction

Nowadays a number of research groups put a great effort into their work to achieve new organic materials with desired properties and better parameters, as well as develop new solutions to be implemented in certain applications, such as sensors, photovoltaics, electroluminescent diodes, lasers, switches and others [1–4]. One of the very promising, and still not enough investigated, group of organic dyes for photonic purposes is pyrazolines. The synthesis and properties of 3-(2,2-dicyanoethenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (DCNP), was patented by Gordon and Bothwell [5] and in the same year published for the first time by group of Allen [6]. The compound became a very attractive organic photonic material due to its great nonlinear optical (NLO) and electro-optic response. A lot of further studies concerning NLO [7,8] as well as light amplification properties of DCNP were done 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, 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 part and various electron-withdrawing moieties conjugated by a double bond. Basing on chosen compounds from the dyes family we have shown their high potential in NLO purposes (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 switching (measurements of completely reversible photoinduced birefringence) [14,15].

In this paper we show the synthetic route for two new derivatives of 1-phenyl-2-pyrazoline,  $\pi$ -conjugated with *ortho*- or *meta*-substituted nitrophenyl group as an electron acceptor, and characterize their 3rd order NLO response (THG), as well as basic spectroscopic properties. In order to emphasize the role of the heterocyclic fragment in observed NLO behavior, we compare the dyes with similar in the electron acceptor part stilbene derivatives,

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where 1-phenyl-2-pyrazoline was substituted by *para*-(dimethylamino)phenyl donor group. Obtained results show significant influence of the electron donor part on measured 3rd order nonlinear susceptibilities. Moreover, taking into consideration also the earlier described third pyrazoline isomer (*para*-nitrophenyl derivative [16]), we can find a correlation between chemical structure (position of the electron-acceptor moiety as well as the type of electron-donor unit) and NLO response coming from series of isomers and derivatives, what can be useful in molecular design of chromophores with desired properties. The chemical structures of the synthesized compounds are shown in Fig. 1.

## 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).

### 2.1. Synthesis

#### 2.1.1. Synthesis of the 1-phenyl-2-pyrazoline-3-carboxyaldehyde

This compound was prepared with 37–52% yield, according to the literature procedure [8,14].  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.12 (t, 2H,  $\text{CH}_2$ ,  $J = 11.6$  Hz), 4.08 (t, 2H,  $\text{CH}_2$ ,  $J = 11.6$  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);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.41 ( $\text{CH}_2$ ), 49.53 ( $\text{NCH}_2$ ), 114.34, 122.49, 129.44, 142.45, 149.38, 185.80 (CHO).

#### 2.1.2. Synthesis of diethyl 2-nitrobenzylphosphonate and diethyl 3-nitrobenzylphosphonate

A mixture of 2- or 3-nitrobenzyl bromide (5.4 g, 0.025 mol) and triethyl phosphite (16.6 g, 0.10 mol) was stirred and heated at about 150–160 °C (oil bath temperature) for 1 h with continuous distillation of the ethyl bromide produced. The reaction mixture was cooled to room temperature and evaporated to dryness (20 mmHg, boiling water bath). Obtained residue was dissolved in ethyl acetate

(100 ml) and washed with saturated solution of  $\text{NaHCO}_3$  ( $6 \times 30$  ml). The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. Obtained thick oily residue was washed with petroleum ether ( $5 \times 20$  ml) and the finally dried in vacuum ( $\sim 5$  mmHg) yielding diethyl 2-nitrobenzylphosphonate (5.4 g, 79%) and diethyl 3-nitrobenzylphosphonate (5.6 g, 82%) as yellow oils. After confirmation of its structure by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy, both compounds were used in the next step without further purification. NMR spectra of crude diethyl 2-nitrobenzylphosphonate [19,20] and diethyl 3-nitrobenzylphosphonate [21,22] were in accordance with literature data.

#### 2.1.3. Synthesis of AM-*o* $\text{NO}_2$ , AM-*m* $\text{NO}_2$ stilbenes and PY-*o* $\text{NO}_2$ , PY-*m* $\text{NO}_2$ 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 anhydrous DMF (20 ml) and anhydrous EtOH (20 ml) a solution of EtONa (15 mmol) in ethanol was added dropwise over 30 min. Obtained reaction mixture was stirred upon cooling for 1 h and next left standing overnight at room temperature. Afterward, a reaction mixture was poured into a cold water (200 ml) and stirred for 30 min.

In the case of stilbenes, AM-*o* $\text{NO}_2$  and AM-*m* $\text{NO}_2$ , the aqueous phases were extracted with dichloromethane ( $1 \times 50$ ,  $3 \times 20$  ml) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and obtained crude products were purified as indicated. Crude AM-*o* $\text{NO}_2$  was purified using short-column chromatography (silica gel, AcOEt) and further recrystallized from diethyl ether, while AM-*m* $\text{NO}_2$  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-*o* $\text{NO}_2$  and PY-*m* $\text{NO}_2$ , the precipitated solids were filtered off, washed with water ( $5 \times 20$  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.

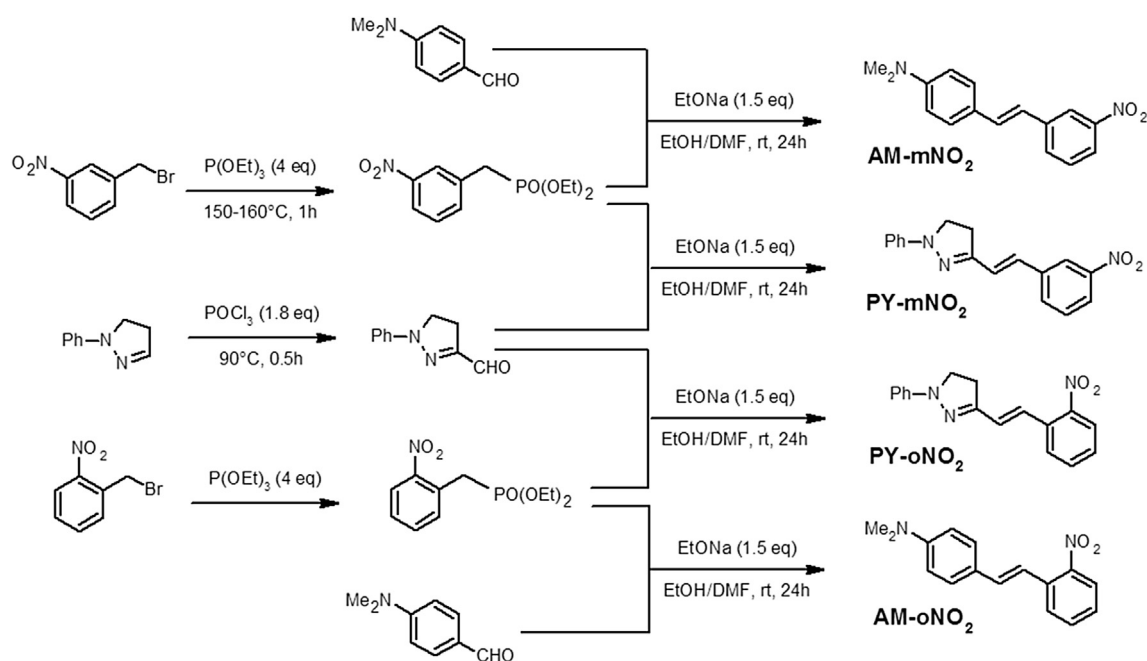


Fig. 1. Synthetic route for the new push-pull type pyrazoline dyes and their stilbene counterparts.

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