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# Synthesis, optical and nonlinear optical properties of new pyrazoline derivatives

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ABSTRACT

We report on synthesis and optical properties of new organic compounds based on substituted pyrazole ring. The investigated pyrazoline derivatives (PRDs) exhibit efficient broadband photoluminescence which covers nearly whole visible spectrum. The experimental results are compared to quantum chemical calculations. Amplified spontaneous emission and photodegradation measurements were performed for hybrid systems based on selected PRDs doped into poly(methyl methacrylate) matrix proving the potential utility of such systems in lasing applications. Two-photon absorption (TPA) properties were characterized by the femtosecond Z-scan technique.



## 1. Introduction

Multifunctional materials, which can be used in modern technology applications are nowadays one of the main research topics in materials science. Modern photonics requires effective materials, which among others can exhibit sizable nonlinear optical effects making them suitable for applications involving in numerous multidisciplinary areas, such as photodynamic cancer therapy [1], multiphoton fluorescence and biological imaging [2], optical power limiting [3], in construction of organic light-emitting diodes [4] or two-photon microfabrication [5]. The materials intended for various applications should also possess other properties, like e.g. good photostability or high efficiency of performing the intended function, e.g. high yield of singlet oxygen production, efficient fluorescence, etc.

We have been interested in synthesis, luminescent and nonlinear optical properties of new derivatives of pyrazoline. Nonlinear optical properties of some pyrazoline derivatives have been already investigated and, in particular, their efficient two- and three photon absorption (2PA and 3PA) together with their potential for lasing [6–10] have been demonstrated. High fluorescence quantum yield, thermal, and photochemical stability make this class of compounds promising for organic thin film laser applications.

In this paper we present studies of a group of newly synthesized pyrazoline derivatives, with respect to their luminescent properties and possible applications in devices fabrication exploiting amplified spontaneous emission/lasing phenomena and two-photon absorption.

The new synthesized derivatives of pyrazoline due to presence of π-conjugated bonds can exhibit high values of dipole moment and hyperpolarizability, which are desired attributes for nonlinear optics and luminescent chromophores. The strategy of its properties modification during molecular design and synthesis is based on structural changes like surrounding electron-donor and acceptor group position manipulation and its capability of effective charge transfer.

## 2. Materials synthesis and methods

We present here the particular steps of synthesis for the investigated pyrazoline derivatives. An intermediate, 1-phenyl-4,5-dihydro-1H-pyrazole, was synthesized by the method of Knoevenagel and Fischer [11]: phenylhydrazine (100 g, 0.92 mol) was dissolved in ether (500 $cm^3$) and cooled down to about 5 °C. Solution of propenal (40 g, 0.71 mol) in ether (100 $cm^3$) was added

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drop wise within 30 min with stirring. The reaction mixture was stirred for the next 48 h. The ether was evaporated and 600 $cm^3$ of 7% sulfuric acid was added. Subsequently it was steam distilled. The 1-phenyl-4,5-dihydro-1H-pyrazole was collected as yellow oil then it solidified and was filtered. Crystallization from petroleum ether gave 17 g (0.097 mol) of 1-phenyl-4,5-dihydro-1H-pyrazole with reaction yield equal to 12.6%. The next step of synthesis was to receive the 1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carbaldehyde (Fig. 1.) as intermediate for other pyrazoline derivatives (Figs. 2–4). $POCl_3$ (32 g, 0.21 mol) was added to DMF (120 $cm^3$) at room temperature. Next, the entire solution of 1-phenyl-4,5-dihydro-1H-pyrazole in DMF (20 $cm^3$) was added to the previously prepared mixture. The whole mixture was heated to 90 °C and kept at this temperature for 30 min and then poured onto water with ice and the product separated overnight as yellow needles. It was filtered and crystallized from a small amount of ethanol. Filtration gave 7.5 g (37%) of 1-phenyl-4,5-dihydro-1H-pyrazole-3-carbaldehyde.

The synthesis procedure for the (*E*)-2-(4-(2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzylidene)malononitrile was performed by the following steps (Fig. 2). At first 2-(4-(bromomethyl)benzylidene)malononitrile was prepared. Then 4-methylbenzaldehyde (30 g, 0.25 mol) and malononitirile (16.5 g, 0.25 mol) were dissolved in 300 $cm^3$ of dry ethanol and sodium acetate was added (0.5 g, 0.006 mol). The reaction mixture was heated under reflux for 4 h. The dark-brown solution was poured onto water with ice and gray precipitate was filtered and dried. The final compound was crystallized twice from ethanol. The yield of this step was 33 g (78.5%). Dry compound was suspended in anhydrous $CCl_4$ with equimolar amount of NBS (35 g, 0.19 mol) and 0.3 g of AIBN as initiator. The reaction flask was heated to the boiling temperature and stirred for 24 h. Colorless succinimide was filtered off and the solvent was evaporated. The residue was crystallized from ethanol. The yield of 2-(4-(bromomethyl)benzylidene)malononitrile synthesis was 32 g (66%). Product from the last step (0.5 g, 2 mmol) and triphenylphosphine (0.524 g, 2 mmol) were dissolved and boiled in dry benzene overnight. Resulting salt was filtered, washed with hot benzene and used without further purification. Sodium ethanolate (0.108 g, 2 mmol) was added to the suspension of phosphonium salt in dry THF (25 $cm^3$), under inert atmosphere at room temperature. The color of the solution became deep red and then the solution was stirred for another 30 min. After that time the solution of 1-phenyl-4,5-dihydro-1H-pyrazole-3-carbaldehyde (0.348 g, 2 mmol) in dry THF (10 $cm^3$) was added drop wise. It was stirred overnight at 50 °C. The solvent was evaporated and to the dark red residue DCM was added, until it became homogenous. The product was purified on silica gel with DCM as eluent and crystallized from ethanol. The yield of synthesis of (*E*)-2-(4-(2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzylidene)malononitrile was 0.318 g (48.5%).

The synthesis procedure of (*E*)-2-(2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzonitrile (PY-oCN) was performed by the following steps (Fig. 3). At first 2-(bromomethyl)benzonitrile was synthesized also as an intermediate for the next pyrazoline derivative (PY-oCNCN). First 2-methylbenzonitrile (25 g, 0.21 mol) was dissolved in 150 $cm^3$ of $CCl_4$. Equimolar amount of NBS and 0.3 g of AIBN were added. The reaction mixture was refluxed for 5 h and after cooling to 40 °C it was filtered and the solvent was evaporated. The residue was chromatographed on silica gel with DCM as eluent. Only the first fraction was collected. The yield of reaction was 25 g (57%). According to the following procedure final compound – (*E*)-2-(2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzonitrile was obtained. The 2-(bromomethyl)benzonitrile from the first step of synthesis described above (0.4 g, 2 mmol) and triphenylphosphine (0.524 g, 2 mmol) were dissolved and boiled in dry benzene overnight. The resulting salt was filtered, washed with hot benzene and used without further purification. To the suspension of phosphonium salt in dry THF (25 $cm^3$), under inert atmosphere at room temperature, sodium ethanolate (0.108 g, 2 mmol) was added. The color of the mixture became deep red and after that the solution was stirred for another 30 min. After that time the solution of 1-phenyl-4,5-dihydro-1H-pyrazole-3-carbaldehyde (0.348 g, 2 mmol) in dry THF (10 $cm^3$) was added drop wise and was stirred overnight at 50 °C. Next the solvent was evaporated and DCM was added to the orange residue until it became homogenous. The product was purified on silica gel with DCM as eluent. It was crystallized from heptane with yield of reaction 0.325 g (59.5%). To obtain – (*E*)-2-(1-cyano-2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzonitrile, which is a derivative of PY-oCN, it was necessary to synthesize another intermediate. The 2-(bromomethyl)benzonitrile (5 g, 25.5 mmol), which was obtained before, was dissolved in a mixture of ethanol (50 $cm^3$) and water (10 $cm^3$). Potassium cyanide (2.6 g, 40 mmol) was added to this solution. Then it was refluxed for 1.5 hand subsequently poured onto ice. Deep green-blue solution was extracted with DCM. The extract was dried with $MgSO_4$ and passed on alumina(neutral) in DCM to give yellowish solution. The eluent was evaporated and the residue crystallized from methanol. The yield of the intermediate was 1.2 g (33%). The last step of (*E*)-2-(1-cyano-2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzonitrilesynthesis was as follows (cf. Fig. 3). Anhydrous sodium acetate was added (0.05 g) to the solution of 2-(cyanomethyl)benzonitrile (0.4 g, 2.8 mmol) and 1-phenyl-4,5-dihydro-1H-pyrazole-3-carbaldehyde (0.490 g, 2.8 mmol), in dry ethanol. Then it was stirred and refluxed overnight. The solvent was evaporated and oily residue was chromatographed on silica gel with DCM as eluent. After evaporation of DCM the oil was dissolved in boiling heptane. After cooling below 0 °C the orange solid precipitated from the solution and then it was filtered. The yield of this synthesis was 0.216 g (efficiency: 26%).

The intermediates: 2-(4-nitrophenyl)acetonitrile and 2-(4-nitrophenyl)acetic acid were synthesized by known procedures. Compound (*E*)-3-(4-nitrostyryl)-1-phenyl-4,5-dihydro-1*H*-pyrazole(PY-p$NO_2$) was made as follows (c.f. Fig. 4). A few drops of piperidine were added to the solution of 2-(4-nitrophenyl)acetic (0.4 g, 2.2 mmol) and 1-phenyl-4,5-dihydro-1H-pyrazole-3-carbaldehyde (0.384 g, 2.2 mmol) in dry ethanol. The whole mixture was mixed and refluxed overnight. The day after, the solvent was evaporated and the residue was dissolved in DCM until the solvent became homogenous. The whole solution was then purified by column chromatography (silica, DCM) and red solid was crystallized from heptane. The yield of this synthesis was 0.110 g (17%). The scheme of (*E*)-2-(4-nitrophenyl)-3-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)acrylonitrile(PY-oCN$NO_2$) synthesis is presented in Fig. 4. The second step is similar to synthesis of PY-p$NO_2$compound. A few drops of piperidine were added to the

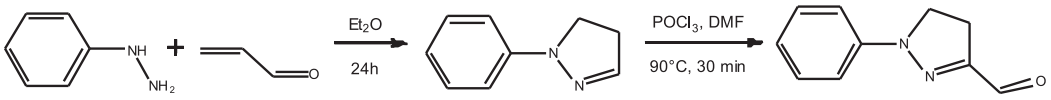


**Fig. 1.** Steps of synthesis of 1-phenyl-4,5-dihydro-1H-pyrazole-3-carbaldehyde.