

## New organic binary solids with phenolic cofomers for NLO applications



Sergiu Draguta<sup>a</sup>, Marina S. Fonari<sup>a,b</sup>, Evgenia Leonova<sup>a</sup>, Tatiana V. Timofeeva<sup>a,c,\*</sup>

<sup>a</sup> Department of Biology and Chemistry, New Mexico Highlands University, Las Vegas, NM 87701, USA

<sup>b</sup> Institute of Applied Physics Academy of Sciences of Moldova, Academy str., 5 MD2028, Chisinau, Republic of Moldova

<sup>c</sup> ITMO University, St. Petersburg 197101, Russia

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### ABSTRACT

Five binary adducts between N,N-dimethyl-4-[(E)-2-(pyridin-4-yl)ethenyl]aniline **1**, N,N-diethyl-4-[(E)-2-(pyridin-4-yl)ethenyl]aniline **2**, N,N-dimethyl-4-[(E)-pyridin-3-ylidiazanyl]aniline **3**, and cofomers that include 4-nitrophenol **I**, 4-nitrobenzoic acid **II**, benzene-1,3-diol **III**, and 2,4-dinitrophenol **IV** were synthesized to follow the factors influencing the formation of polar crystals. New solids were characterized by melting points and absorption spectra, while their structures were proven by single crystal X-ray diffraction. Adducts differ by the components' ratio and position of the acidic hydrogen atom, thus giving examples of four new cocrystals and one salt. The single crystal X-ray analysis revealed the acentric packing for two compounds, **1 (I)** and **3(III)** that crystallize in the  $Pca2_1$  and  $P1$  space groups. The melting point data and the cut-off wavelength from absorption spectra show that these materials are stable till relatively high temperatures and transparent in a wide range of spectrum.

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### 1. Introduction

The search for new materials for non-linear optics (NLO) remains in focus of crystal engineers for decades [1–4]. Organic compounds with extended conjugated system between the donor and acceptor groups are good candidates for NLO due to their high molecular hyperpolarizability, fast electronic response and thermal stability [2]. In order to be NLO active, noncentrosymmetric molecular packing is required. The formation of the acentric hydrogen-bonded systems was suggested by M. Etter as the prerequisite for the acentricity in organic solids and was confirmed by the nitroaniline and urea-containing crystals [5–8]. It was also proven that organic salts demonstrate the higher values of molecular hyperpolarizability compared to cocrystals that comprise the neutral components [9]. The discovery of 4-(4-(dimethylamino)styryl)-1-methylpyridinium-4-methylbenzenesulfonate (DAST) [10–12] with strong Columbic interactions between the charged dipole entities has opened a modern era of NLO materials, being generated by the slight modifications of the DAST components, 4-(4-(dimethylamino)styryl)-1-methylpyridinium-4 cation and

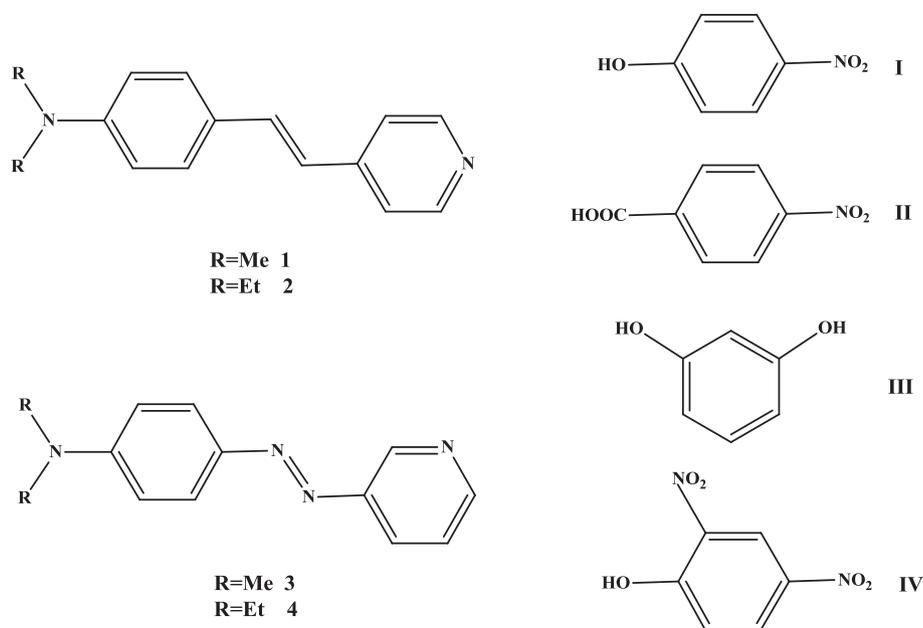
methylbenzenesulfonate anion [13–18].

We have recently reported the acentric binary crystalline organic solids composed of different aminopyridines and 4-nitrophenol [19]. The combination of these components resulted in strong hydrogen bonding and the proton transfer that increases the molecular hyperpolarizability [19–21]. In the 4-nitrophenol molecule the phenolic group exhibits amphoteric properties acting as hydrogen-bond donor through the hydroxyl H-atom, and electron-donor as well through the oxygen atom lone pair, while the nitro-group is displaying the electron- and hydrogen-bond acceptor properties. In the present work we combine 4-nitrophenol **I**, and its analogues and derivatives, 4-nitrobenzoic acid **II**, 1,3-benzene-diol **III**, and 2,4-dinitrobenzene diol **IV** with the chromophores that differ from the previously reported by us amino- and N-methylaminosubstituted pyridines [19,22], by possessing longer conjugation system. These base compounds include N,N-dimethyl-4-[(E)-2-(pyridin-4-yl)ethenyl]aniline **1**, N,N-diethyl-4-[(E)-2-(pyridin-4-yl)ethenyl]aniline **2**, and N,N-dimethyl-4-[(E)-pyridin-3-ylidiazanyl]aniline **3**, and together with the cofomers used in this study are shown in Scheme 1.

Contrary to the reported series of DAST compounds, the non-substituted pyridine nitrogen atom in all these bases provides an opportunity for the hydrogen bonding and donor-acceptor charge transfer. The choice of cofomers is explained on one hand by the

\* Corresponding author. Department of Biology and Chemistry, New Mexico Highlands University, Las Vegas, NM 87701, USA.

E-mail address: [tvtimofeeva@nmhu.edu](mailto:tvtimofeeva@nmhu.edu) (T.V. Timofeeva).



**Scheme 1.** Schematic notation for compounds used in this study.

presence in all of them the strong H-donor in the form of hydroxy group capable to generate the robust  $\text{OH}\cdots\text{N}(\text{pyridine})$  heterosynthon [23], and on the other hand by the fact that the crystals of the pure forms of 1,3-benzene-diol **III** [24], 2,4-dinitrophenol **IV** [25–27], and several of their adducts are acentric solids [28,29] studied as NLO materials [30]. By changing the position of the pyridine nitrogen atom, N-substituents, and bridge in chromophores on one hand, and the cofomers on the other hand, we tried to understand the outcome of these changes along with influence of functional groups on the acentric crystal packing. In this paper we also present the newly synthesized N,N-dimethyl-4-[(E)-pyridin-3-ylidiazonyl]aniline **3** [31], and its acentric adduct with benzene-1,3-diol **III**. According to the early data, the azo chromophores similar to **3** and **4** (recently reported by us) [32] can display additional useful properties such as enhanced thermal, oxidative, and photochemical stability. In addition, the [(aminophenyl)azo]-pyridinium moieties should be resistant to the degradative [2 + 2] cycloaddition pathways [23,33] that present potential complications in some stilbazolium systems resulting in the reduced NLO activity [34]. Furthermore, the altered position of pyridine nitrogen atom in **3** and **4** compared with **1** and **2** might impose additional asymmetry in the generated hydrogen-bonding patterns assisting acentric crystal packing.

## 2. Results and discussion

### 2.1. General

The combination of starting materials (Scheme 1) has resulted in five binary solids, **1** (**I**), **2** (**II**), **2**(**2**) (**III**), **3**(**3**) (**III**) and **3** (**IV**), including two polar crystals, **1** (**I**) and **3**(**3**) (**III**) that crystallize in the acentric space groups  $Pca2_1$  and  $P1$ , respectively. No adducts with **4** were obtained so far. The main crystallographic data for new compounds are summarized in Table 1, the hydrogen bond parameters are given in Table 2. Except for **1** and **1** (**I**), that are orange, all other starting chromophores and the final adducts are red solids (Fig. 1). The plot in Fig. 2 combines the melting points for the starting materials and the final products. It demonstrates thermal stability of adducts since their melting points are ranging from 185(2) to 245(2) °C, approaching corresponding values for the initial bases.

### 2.2. Crystal structures

N,N-dimethyl-4-[(E)-pyridin-3-ylidiazonyl]aniline **3** (Fig. 3a) crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$  contrary to the recently reported by us N,N-diethyl-4-[(E)-pyridin-3-ylidiazonyl]aniline **4** that crystallizes in the acentric  $P2_12_12_1$  space group [32]. Similar to **4**, molecule **3** adopts a *trans*-conformation with respect to the diazo  $\text{N}=\text{N}$  bond. The twisted shape of the molecule is described by the dihedral angle between the benzene and pyridine rings of 21.56(5)° [8.03 (5)° in **4**]. The T-shape arrangement of the molecules in crystal is reinforced by the weak  $\text{C}(1)\text{H}\cdots\text{N}(2)$  hydrogen bond (2.56, 3.343(2) Å, 142°) with participation of the bridging N-atom that supports the stair-case chains. The chains are running along the crystallographic  $c$  axis. The dihedral angle between the neighboring molecules in chain is 89.83(1)°. The antiparallel packing of these chains provides the stacks of the molecules with the alternating interplanar separations of 3.53 and 3.64 Å (Fig. 3b). Our CSD search [35] revealed no similar  $\text{CH}\cdots\text{N}$  interactions with participation of the bridging nitrogen atoms in the relative structures [36,37].

Analysis of the difference Fourier maps at the latest stages of the refinements for the adducts described below allowed to unambiguously locate the positions of functional hydrogen atoms, and to conclude that four adducts, **1** (**I**), **2** (**II**), **2**(**2**) (**III**), **3**(**3**) (**III**) are cocrystals with no proton transfer, and only one, **3** (**IV**) represents an organic salt, since the proton transfer occurs from the phenoxy group to the pyridine N-atom. Two of these adducts, **1** (**I**) and **3**(**3**) (**III**) crystallize in the acentric space groups,  $Pca2_1$  and  $P1$ , respectively, and three, **2** (**II**), **2**(**2**) (**III**) and **3** (**IV**) crystallize in the centrosymmetric space groups. The stoichiometric ratios are primarily dictated by the number of H-donor (hydroxy) groups in the acidic molecules, being the expected 1: 1 in **1** (**I**), **2** (**II**), and **3** (**IV**), 2: 1 in **2**(**2**) (**III**), and an unusual 3: 1 in **3**(**3**) (**III**).

Adduct **1** (**I**) crystallizes in the non-centrosymmetric orthorhombic  $Pca2_1$  space group. In the binary formula unit neutral molecules are held together *via* single  $\text{OH}\cdots\text{N}$  hydrogen bond,  $\text{O}\cdots\text{N}$  2.681(3) Å (Fig. 4a, Table 2) that provides an insignificant twist within the adduct described by the dihedral angle of 14.9(5)° between the mean planes of the skeletons of the molecules. The hydrogen bond that acts in a head-to-tail mode affords a linear and

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