



Contribution to molecular mechanism of optical nonlinearity and electric conductivity of 3-nitroaniline single crystals by dielectric, electric and quantum chemical studies

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ABSTRACT

The measurements of electric permittivities, of electric DC conductivity, and of the current–voltage characteristics at various temperatures and field frequencies were performed for the single crystals of 3-nitroaniline (m-NA). The 1.77 eV energy gap in the band structure, calculated by quantum chemical methods, is compared with the electronic transitions energies known from literature and with the experimentally found 0.40 eV activation energy of conductivity. The sign reversal of the current during the switch-on/off of the 980 nm diode laser beam and of the applied voltage seems to originate from the electrooptic Pockels effect and to be connected with the dynamical disorder in the crystal. The appearance of the current confirm the generation and detrapping of charge carriers (polarons) by near IR (NIR) radiation. These data indicate the electret features of the crystal. The mechanisms of electric conductivity and optical nonlinearity in the solid m-NA are proposed.

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1. Introduction

The mechanism of charge carriers generation and their transport in organic solids is still intensively studied due to the continuous interest in new materials for molecular electronics and photonics. Electric conductivity is a property of the charge transfer (CT) complexes like e.g. TTF-TCNQ [1,2], of one-component molecular crystals like TCNQ [3] and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) [4–7] or polymers like polyanilines [8], poly(paraphenylene-vinylene) (PPV) [9], poly(biphenyl-methylsilyle) (PBMSi) [10], and of DNA molecule [11–14]. In order to understand the conductivity, collective excitations like excitons [1,4–7], polarons [1,2,9,10], bipolarons [2] and solitons [2] as well as the structural disorder [9–12] are taken into consideration.

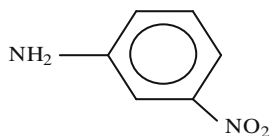
Nitroanilines, simple polar organic compounds with the electron-donor amino group and the electron-acceptor nitro group attached to the benzene ring, reveal very weak electric conductivity and involved EPR signals in the crystals grown from ethanol solution [15]. The EPR signals were as well recorded in the m-NA (Scheme 1) single crystals grown from melt. These signals considerably increased after the exposure to near IR (NIR) radiation and/or heating above 320 K [16].

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The polarized IR reflection spectra enabled to recognize the partly “ionic” or “metallic” character of m-NA single crystals and to determine the so called “effective charges” ($\delta\mu/\delta q$), and the vibrational contributions to electric permittivity in all crystallographic **a**, **b** and **c** directions [17]. The spectroscopic studies were performed in the frame of search for a relationship between vibrational spectra and optically nonlinear (NLO) properties of the m-NA crystal [17–21]. It crystallizes in the noncentrosymmetric orthorhombic mm2 space group [22,23] (Fig. 1) what lies also at the origin of its pyroelectricity [24], piezoelectricity [25], ferroelectric features [26], and recently detected terahertz emission [27,28].

Two phase transitions, none of the first order, were found by differential scanning calorimetry (DSC), ¹H NMR and dielectric methods: the low-temperature one (at ~140 K) from glassy to rotative phase (on heating) and the high-temperature one from rotative to plastic phase at 365 K. The decrease of the ¹H NMR relaxation time T_1 of the m-NA powder upon low-intensity low-energy radiation has been rationalized by the photochemical NIR generation of paramagnetic species. The temperature and frequency dependences of the electric permittivity pointed out on a conductivity contribution to the dielectric losses above 330 K [29]. The variable temperature structural studies confirmed the two transformations occurrence, revealed the anomalous contraction along the **b** crystallographic axis, characterized the N–H...O,



Scheme 1. Molecular structure of meta-nitroaniline.

N–H...N, C–H...O hydrogen bondings, and detected the large amplitude motions of the $-\text{NO}_2$ group in the m-NA crystal [23]. To explain the NIR influence and the conductivity of the m-NA crystal the hypothesis has been proposed that the NIR radiation excites the overtones of $-\text{NH}_2$ stretching vibrations which couple via proton transfer along the N–H...O hydrogen bonding with the electronic transitions lying in the NIR region [16,29]. It seems that like in the conducting polyanilines [30] this coupled excitation propagates through the crystal as a charged polaron. The variable temperature polarized FT-NIR spectra revealed two kinds of polarons in the m-NA single crystals: (i) generated by the NIR radiation, and (ii) thermally generated, and the autocatalytic character of the polaron formation [31]. The polarized UV-Vis electronic absorption spectra of the m-NA single crystals were measured and calculated [by a self-consistent field (SCF) ab initio method] by Bendazzolli et al. [32]. The linear electrochromic effect (electroabsorption spectra) and three main low frequency dielectric permittivities were reported by Stevenson et al. [33]. The low-temperature photoluminescence spectra of the m-NA single crystal and solid solution, and the calculations of electronic transitions were the subjects of two papers by Szostak et al. [34,35]. The fluo-

rescence band maximum, strikingly red shifted with respect to the one of phosphorescence, was attributed to the m-NA radical anions – negatively charged polarons – in accord with the calculated doublet–doublet D_0 – D_1 transition value. Due to the much larger hyperpolarizability, β , of the m-NA radical anion than of the neutral molecule these polarons are relevant to the NLO properties of the crystal [34].

The goal of this work is to check whether the NIR radiation actually generates charge carriers, or/and, in the language of conductivity specialists, whether it releases charge carriers from traps in the m-NA crystal. We aimed also to throw more light on the electric properties of m-NA single crystal in the context of its disorder [16,23,29] and the previous findings [15–17,24–26,31,34,35] by the variable temperature and frequency studies of its dielectric properties, by the temperature and field dependences of the m-NA DC electric conductivity and by means of the quantum chemical calculations of its band structure.

2. Experimental methods

Commercial (Reachim) m-NA was purified by the multiple zone refinement and single crystals were obtained from melt by the Bridgman method. Two single crystal plates were cut along the **bc** (1 0 0) cleavage plane but only one was enough stable due to its quite large dimensions: 0.4 mm thick with (9×6) 54 mm² area, and it was used in the below described experiments.

The electric measurements were carried out in Novocool Criostat in the temperature range between 173 K and 323 K. The dielectric measurements, presented in Figs. 2 and 3 were

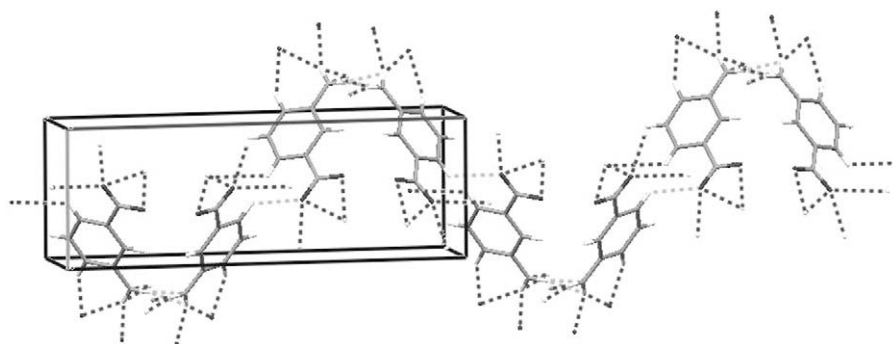


Fig. 1. Projection of the m-NA crystal unit cell.

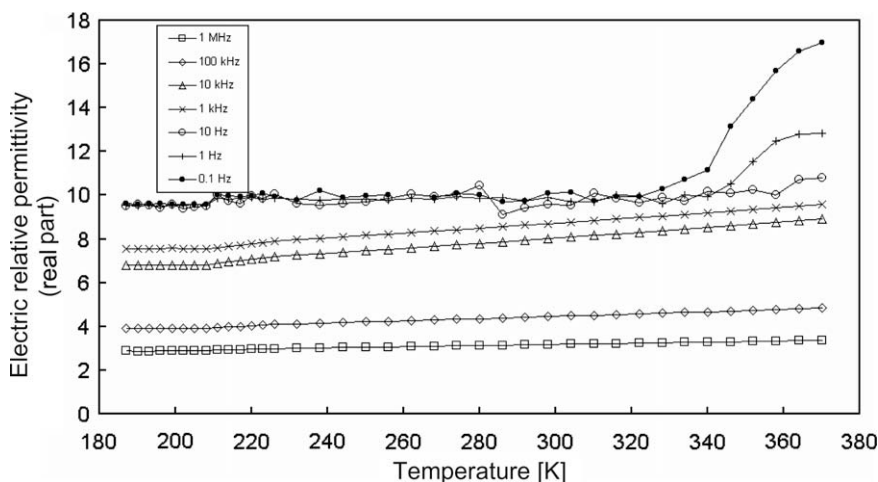


Fig. 2. Temperature dependence of the real part of relative electric permittivity (dielectric constant) of m-NA crystal at various frequencies.

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