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Solid-state polarized IR-spectroscopic study of high temperature red phase of 5-amino-2-methoxypyridine ester amide of squaric acid ethyl ester

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Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

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5-Amino-2-methoxypyridine ester amide of squaric acid ethyl ester is stabilized into two stable solid phases depending on the temperature. Yellow solid phase, which crystallizes at T = 298K, is characterized with noncentrosymmetric space group *Cc,* a pseudo-layer structure with molecules linked by moderate NH…O=C intermolecular hydrogen bonds (2.955 Å). Amorphous red solid phase is obtained as a result of phase transition at 200ºC, which structure and IR-spectroscopic elucidation is performed by means of linear-polarized IR-spectroscopy of oriented colloid suspensions in nematic mesophase.

Key words: IR-LD spectroscopy, colloid suspension, structural elucidation, high temperature solid phase.

INTRODUCTION

Electro-optical and nonlinear optical properties of organic molecules and crystals are of great interest for applications in the communication technology, owing to the tendency to replace classical electronic materials with suitable organic crystals [1–3]. In some cases squaric acid derivatives display a possibility to crystallize in noncentrosymmetric space groups, meaning that such compounds can exhibit second order NLO properties in the bulk. This prompts us to design novel squaric acid derivatives with heterocyclic compounds. 5-Amino-2-methoxypyridine ester amide of squaric acid with second order NLO application in bulk has been synthesized, spectroscopically and structurally elucidated by means of single crystal X-ray diffraction, solid-state linear polarized IR-spectroscopy, UV-spectroscopy, mass spectrometry, and thermal methods [4]. At room temperature (solid phase 1, Scheme 1) the compound crystallizes in the noncentrosymmetric space group *Cc* and exhibits a pseudo-layer structure with molecules linked by NH…O=C intermolecular hydrogen bonds with length of 2.955 Å and NH…O angle of 153.41º, respectively. The performed thermal analysis (Fig. 1) has been shown [4] that an initial distinct endothermic process followed by two overlapping exothermic calorimetric peaks takes place during heating. The endothermic peak with T_{max} = 143.5ºC has been associated with substance melting with an enthalpy of 155 J/g. The next broad exothermic DSC effect, which is partially overlapped with a second exothermic process, has been associated with a larger enthalpy change. The second exothermic process has ended at 200ºC, with a formation of second red solid phase 2 (Scheme 1). Using the conventional solid-state IR-spectroscopy, it has been proposed new intermolecular NH…N interactions in the last phase.

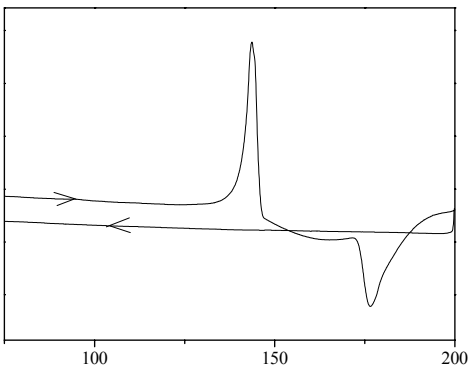

Fig. 1. DSC data of solid phase 1 [4].

In this paper we report IR-spectroscopic and structural elucidation of solid phase 2 by means of a linear-polarized IR-spectroscopy of oriented colloid suspensions in nematic liquid crystal [5–8]. For systems where is impossible to obtain suitable singe crystals for X-ray diffraction study, like the presented one, the spectroscopic method is appeared to be unique for IR-band assignment and obtaining of structural information in condense phase.

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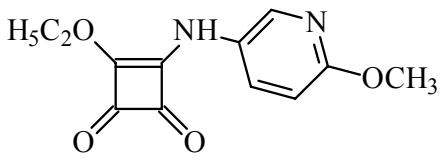
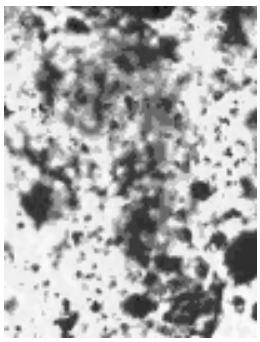
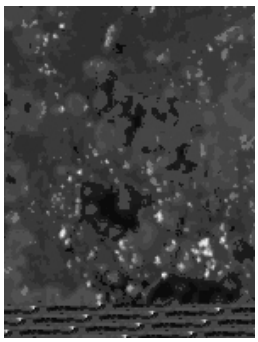




Yellow solid phase 1.



Red solid phase 2.

Scheme 1. Chemical diagram of compound studied; solid phases 1 and 2.

EXPERIMENTAL

Synthesis

The starting compound, 5-amino-2-methoxy-pyridin ester amide of squaric acid ethyl ester (solid phase 1) was synthesized according to the procedure described in [4]. IR and UV-Vis spectroscopy confirmed the purity of the compound. The most intensive signal in the mass spectrum is that of the peak at *m/z* 249.29, corresponding to the singly charged cation $[C_{12}H_{13}N_2O_4]^+$ with a molecular weight of 249.24. The solid phase 2 was obtained by heating of solid phase 1 at 200ºC at Pt-crucible. It was also obtained after heating of the starting compound in glass capillary. Our attempts to receive suitable single crystals of this phase have failed due to the formation of solid phase 1 after dissolving of the solid phase 2.

Materials and methods

IR-spectroscopic measurements within 4000–400 cm^{-1} range were obtained on a Thermo Nicolet 6700 FT-IR spectrometer (resolution 1 cm^{-1}, 250 scans). A Specac wire-grid polarizer was used. Oriented solid samples were obtained as a colloid suspension in a nematic liquid crystal of the 4'-cyano-4'-alkylbicyclohexyl type (ZLI 1695, Merck), mesomorphic at room temperature. Its weak IR-spectrum permits recording of the guest-compound IR-bands in the whole 4000–400 cm^{-1} range. The isolated nitrile stretching IR-band at 2236 cm^{-1} serves additionally as an orientation indicator. The effective orientation of the samples was achieved through the new procedure described in [5–8]. The procedure for the position (v_i) and integral absorbances (A_i) determination for each *i*-peak has been carried out by deconvolution and curve-fitting procedures at 50:50% ratio of Lorentzian to Gaussian peak functions, γ^2 factors about 10^{-5} and 2000 iterations [7, 8]. The means of two treatments were compared by Student *t*-test. The experimental IR-spectral patterns have been acquired and processed by GRAMS/AI 7.01 IR spectroscopy (Thermo Galactic, USA) and STATISTICA for Windows 5.0 (StatSoft, Inc., Tulsa, OK, USA) program packages. The theoretical approach, experimental technique for preparing the samples, procedures for polarized IR-spectra interpretation and the validation of this new linear-dichroic infrared (IR-LD) orientation solid-state method for accuracy and precision have been presented. The influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands, the rheological model, the nature and balance of the forces in the nematic liquid crystal suspension system, and morphology of the suspended particles have been also discussed [6–8].

Spectroscopic and structural results were obtained by the orientation technique [5–8] using the known reducing-difference procedure designated as "stepwise reduction" for polarized IR-spectra interpretation. This method was primarily suggested by Thulstrup and Eggers for polarized UV-spectral interpretation [9]. The procedure consists in consecutive elimination of the spectral bands of a given polarization by means of subtracting the perpendicular spectrum multiplied by a coefficient from the parallel one. This procedure was extended by Spanget-Larsen [10] and by Korte and Lampen [11] to samples orientated in stretched polyethylene and nematic solution, respectively. A systematic analysis of this approach and its application to IR-bands assignment according to their symmetry appurtenance was developed by B. Jordanov and co-workers [12–15] for polarized IR-spectra in nematic liquid crystal solution. The method consists of subtraction of the perpendicular spectrum, (IR_s, resulting from a 90º angle between the polarized light beam electric vector and the orientation of the sample) from the parallel one (IR_p) obtained with a co-linear mutual orientation. The recorded *difference* (IR_p–IR_s) spectrum divides the corresponding parallel (A_p) and perpendicular (A_s) integrated absorbencies of each band into positive values originating from transition moments, which form average angles with the orientation direction (**n**) between 0º and 54.7º (magic angle), and negative ones corresponding to transition moments between 54.7º and 90º. In the *reducing-difference procedure*, the perpendicular spectrum multiplied by the parameter ***c***, is subtracted from the parallel one and ***c*** is varied until at

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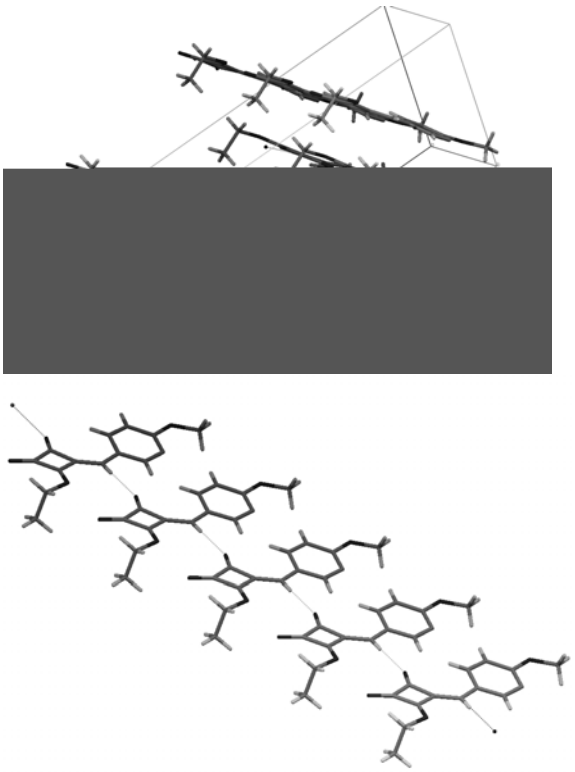
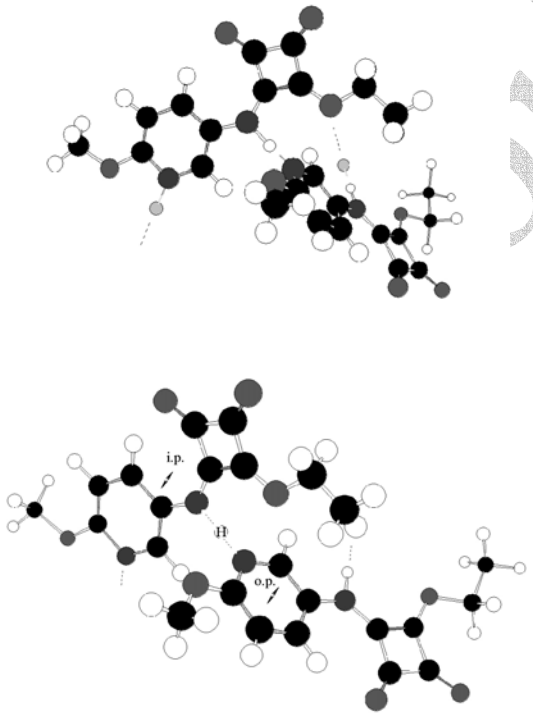


Scheme 2. Hydrogen bonding in solid phase 1.



Scheme 3. Intermolecular interactions in solid phase 2.

Moreover, the absence of well-defined isolated band of ν_{NH}, typical for solid phase 1, and an observation of the broad band within 3500–2500 cm^{-1} as well as the intensive broad band at 1587 cm^{-1}, typical for full or partially charged amines, proposed strong intermolecular NH…N_{Py}, which has been observed in a series of papers dealing with protonated heterocyclics [18–20] or in 4-aminopyridinium hemiperchlorate, where the NH bonds in the NH…N interaction is equalized and H- is fixed at an equal distance of both the N-atoms [21]. Additional confirmation of the last assumption follows as well from the obtained more than 100 nm batochromic sift of λ_{max} in the solid red phase, typical for push-pull systems [1–3].

The above stated vibrational assignment is experimentally proved by the polarized IR-spectroscopic study. Moreover, an interesting result is obtained in addition. In contrast to solid phase 1, where the elimination of o.p. modes leads to a total vanishing of the corresponding IR-bands of same symmetry class [4], the elimination of the corresponding bands in solid phase 2 as well as the $\nu^{s}_{C=O(Sq)}$ stretching modes leads to an observation of second bands of same symmetry class. As can be seen the elimination of each of the well-defined by deconvolution and curve-fitting procedures bands at 1803 and 1795 cm^{-1} leads to an observation of numbering maximum (Figs. 3.2 and 3.3).

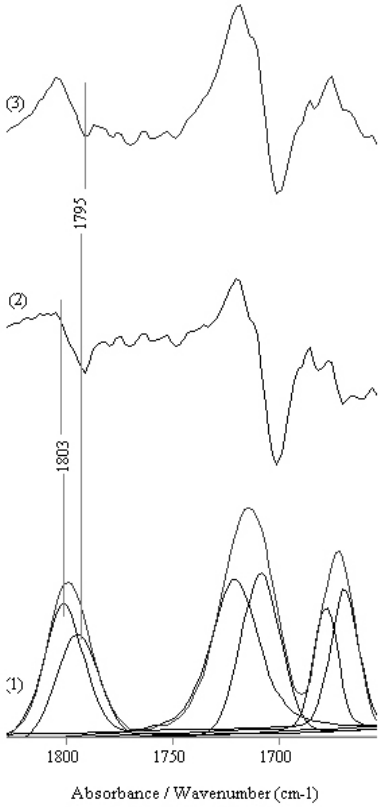


Fig. 3. Curve-fitted IR-spectrum (1) of solid phase 2 (χ^2 values less then 8×10^{-4}) within 1850–1650 cm^{-1} and reducing IR-LD spectra after elimination of the bands at 1803 cm^{-1} (2) and 1795 cm^{-1} (3).

On the other hand, the elimination of the bands about 1600 and 835 cm^{-1} at equal dichroic ratio in

addition confirms the assumption stated above, due to in the frame of one isolated molecule is impossible to be eliminated IR-bands with i.p. and o.p. symmetry classes. This phenomenon has been observed in systems, where the unit cell contains mutual perpendicular oriented molecules [22, 23]. These results proposed that the second phase 2 is characterized by infinite zig-zag chains of molecules, connected by strong NH..N_{Py} hydrogen bonds (Scheme 3). In the frame of these chains the molecule of 5-amino-2-methoxypyridin ester amide of squaric acid ethyl ester is with low influenced conformation, because of our thermal analysis, shows only a small thermal process at 94ºC with shape, indicating a second order phase transformation, explained by the liberation of a rotation around the C–N bond [4].

CONCLUSION

By means of linear-polarized IR-spectroscopy of oriented colloid suspensions in nematic host, the IR-spectroscopic and structural elucidation of the high temperature solid phase of 5-amino-2-methoxypyridine ester amide of squaric acid is preformed. In contrast to the solid phase obtained at room temperature, where a pseudo-layered structure is stabilized by intermolecular NH…O=C intermolecular hydrogen bonds with length of 2.955 Å [4], in the high temperature phase strong NH…N_{Py} interactions are predominant. As a result of the solid phase transition, the layered structure is distorted and infinite zig-zag chains are typical.

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ПОЛАРИЗАЦИОННО ИЧ-СПЕКТРАЛНО ИЗСЛЕДВАНЕ НА ВИСОКОТЕМПЕРАТУРНАТА „ЧЕРВЕНА“ ФАЗА НА 5-АМИНО-2-МЕТОКСИПИРИДИН ЕСТЕР АМИД НА ЕТИЛОВИЯ ЕСТЕР НА КВАДРАТНАТА КИСЕЛИНА

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Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

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(Резюме)

В наша предишна работа бе установено, че съединението 5-амино-2-метоксипиридин естер амид на етиловия естер на квадратната киселина се стабилизира в две твърди фази в зависимост от температурата. Така наречената „жълта“ фаза изкристализира при температура T = 298K и се характеризира с нецентросиметрична пространствена група *Cc,* а молекулите образуват псевдослоеста структура посредством междумолекулни NH…O=C водородни връзки (2.955 Å). Втората, аморфна „червена“ фаза се получава в резултат на фазов преход при температура от 200ºC. Нейното спектрално охарактеризиране бе извършено използвайки възможностите на поляризационната ИЧ-спектроскопия на ориентирани колоидни суспензии в нематичен течен кристал.

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