

Differently coloured crystalline modifications of organic autocomplexes of the nitroaromatic type

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Abstract

The improved methods for preparation of the differently coloured crystalline modifications of the organic intramolecular charge transfer complexes (autocomplexes), having electron acceptor fragments of the nitroaromatic type, have been developed. The preparation of the coloured modifications - yellow, orange and red for N-(p-tolyl)-2,4,6-trinitroaniline - potential nonlinear optical material are carried out under carefully controlled conditions in different organic solvents or their mixtures. The crystalline modifications have been characterized by means IR-spectroscopic data; fluorescence properties of these are described.

Keywords: charge transfer complexes, synthesis, crystalline modifications, infrared spectroscopy, fluorescence

1. Introduction

The organic compounds with intramolecular charge transfer, so-called autocomplexes, where the electron donating and accepting moieties are combined into one and the same molecule, have attracted significant scientific and technological attention over the years. The similar systems, especially with intramolecular proton transfer, are widely used in luminescent materials with anomalous Stokes shift, laser systems and microsondes [1]. The present study investigates differently coloured crystalline modifications, obtained for the autocomplex of trinitroaryl type N-(p-tolyl)-2,4,6-trinitroaniline. Synthesis of this autocomplex has been carried out by the condensation reaction between picryl chloride and the corresponding aromatic amine. Three crystalline forms are involved: yellow, orange and red (Fig. 1). The preparation of these crystalline forms was carried out under carefully controlled conditions in different organic solvents and their mixtures. It is known, that some derivatives of N-picrylaniline can be obtained in differently coloured crystalline forms. However, the existing data cannot allow to make unambiguous conclusions about the nature of these modifications [2].

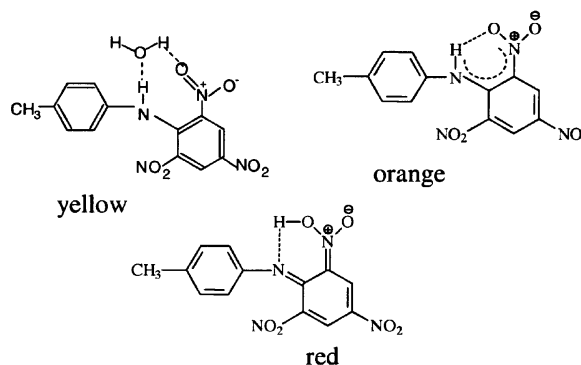


Fig. 1. Molecular structure of crystalline modifications for N-(p-tolyl)-2,4,6-trinitroaniline

2. Experimental

A description for the preparation of the trinitroaryl type autocomplexes, including N-(p-tolyl)-2,4,6-trinitroaniline can be found in our previous paper [3]. Three crystalline forms of this autocomplex were obtained by interaction of the initial reagents, using certain reaction solvents, namely red - from acetone, orange - from ethanol and yellow - from water-acetone mixture.

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Infrared spectra were recorded on a Nicolet FTIR spectrometer 'Avatar', resolution 1 cm^{-1} , 100 scans. For preparing of the samples a standard multiple attenuated total reflection equipment with a ZnSe element was used. Fluorescence spectra were recorded on an Elumin-2M fluorescence spectrophotometer.

3. Results and Discussion

Molecular crystals of N-(p-tolyl)-2,4,6-trinitroaniline display a wealth of crystalline phases, of which some are photoactive while others are photoinert. In this work three different crystalline modifications — red, orange and yellow of this autocomplex were isolated and structurally characterized by means of IR- spectroscopy and fluorescence spectra. We have investigated the solid-state crystalline modifications only. The crystal structure of these forms has been established using X-ray diffraction method. In our previous study in this field [4] we found, that molecular conformations of red and orange forms (crystal of the yellow form suitable for X-ray analysis have not been obtained) differ only slightly and these distinctions cannot cause the observed difference in colour. X-Ray analysis demonstrated also the absence of geometrical prerequisites to the intermolecular charge transfer interaction. In both structures the molecules adopt a herring-bone arrangement, but the neighbouring molecules are arranged head-to-head in the red and head-to-tail in the orange form.

IR spectra have been investigated. The orange and yellow forms have nearly identical spectral characteristic and in the field $3500\text{--}3000\text{ cm}^{-1}$ they coincide. The main differences are manifested between the red and both orange and yellow forms. Possible interpretation of the IR spectra include the following: bands at 3250 cm^{-1} (NH-), 3100 cm^{-1} (CH - aromatic) correspond to the group of orange and yellow forms; band at 3300 cm^{-1} (OH-), 3100 cm^{-1} (CH-aromatic) and 3070 cm^{-1} (CH-quinon) correspond to group of red form. On the other hand all of the three forms display also differences in the NO_2 -group field.

Since the preparation of yellow form is carried out in aqueous solution apparently we can suppose that this form exists as a water-cluster compound. More detailed studies of this phenomenon are in progress.

The analysis of the fluorescence spectra (Fig.2) obtained for solid state crystalline modifications shows that anomalous Stokes shift up to 5000 cm^{-1} , which are found for both orange and yellow forms, differ only slightly in value of their Stokes shifts; the red form exhibits fluorescence with a normal Stokes shift of approximately 1300 cm^{-1} . The large Stokes shifts in these cases are due to the formation of intramolecular proton-transfer reaction in the excited state.

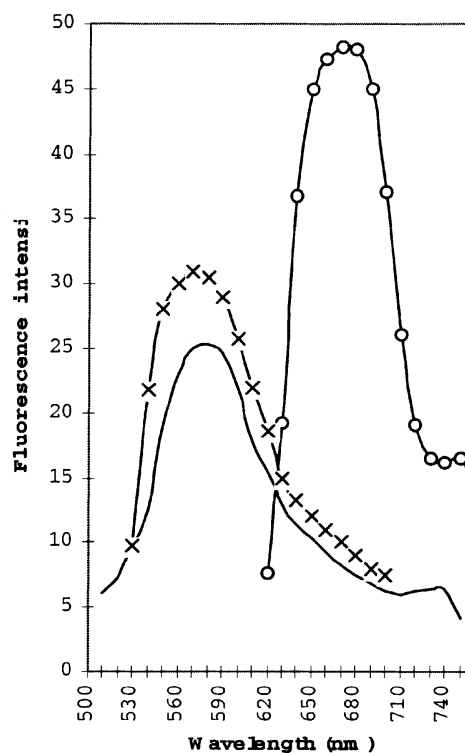


Fig.2. Molecule fluorescence emission spectra of crystalline modifications for N-(p-tolyl)-2,4,6-trinitroaniline: yellow (—), orange (—x—), red (—o—). Excitation at: 460 nm (for yellow and orange form), 600 nm (for red form).

Taken together, these data allow to believe that the nature of the acceptor picrylic ring in autocomplex N-(p-tolyl)-2,4,6-trinitroaniline which cause observed difference in colour is its crystalline modifications.

References

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