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Photochromic properties of the molecule Azure A chloride in polyvinyl alcohol matrix

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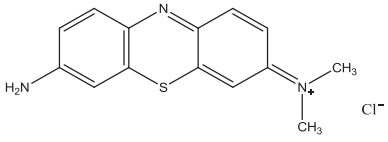
ABSTRACT

In the present work, isomerization, photophysical properties and heat conductivity of the substance Azure A chloride (AZAC): 3-amino-7-(dimethlamino)phenothiazin-5-ium chloride under the action of UV radiation in the presence of polyvinyl alcohol (PVA) matrix was studied using the Hartree-Fock (HF) and Density Functional Theory (DFT) methods. The electronic absorption spectra of AZAC in dimethylformamide (DMF) solution and in aqueous medium before and after UV radiation were calculated. The nature of absorption bands of AZAC and its tautomeric prototropic form with the transfer of the electron ($AZAC_1$) in the visible and near UV spectral regions was interpreted. The solvent effect on the absorption spectrum of the AZAC has established. The comparison of measured FTIR, UV–Visible data allowed assignments of major special features of title molecules. The frontier molecular orbital HOMO-LUMO have been also presented that shows the charge transfer interactions taking place within these molecules. The excitation energies for both molecules AZAC and $AZAC_1$ have also been calculated. The experimental as well as theoretical investigations of azure molecule have a close agreement and it gives other important clues about the properties of the system. Anisotropy of thermal conductivity in PVA-films containing AZAC and $AZAC_1$ were also measured.

1. Introduction

AZAC is a phenothiazine dye available as green to brown powder. It is formed by the oxidation of methylene blue and is strongly metachromatic. It is utilized as a part of making azure eosin stains for blood smear staining. Azure dyes are used as redox mediators for electrochemical biosensing [1].



Azure A chloride is generally used as solvents and colored reagents in numerous experimental and scientific investigations [2]. Estimation of the molecular orbital geometry demonstrate that the visible absorption maxima of such type of molecules correspond to the electron transition from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The structure and the vibrational spectroscopic investigation of the thiazines are critical for the understanding of their physicochemical and pharmaceutical properties. Vibrational spectroscopic studies of

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thiazine dye and its derivatives have been reported in the literature [3]. The solvent effect is closely related to the nature and degree of dye–solvent interactions. The impact of solvent on the aggregate formation of a wide variety of ionic dyes has also been reported by many researchers [4]. The present investigations expect to understand the structural and bonding features and molecular information such as π conjugations, electron delocalization and resonance interaction using UV–Vis calculations. In the prior study, FT-IR, Raman as well as UV–VIS spectra of the phenothiazine dye AZAC have been recorded and examined [1]. The authors have also reported the ability of the TD – DFT method to predict the absorption spectra of a series of oxazine dyes and the effect of solvent on the accuracy of these predictions [5]. Taking into the account of this study, it's clear that in the series of oxazine dyes an accurate prediction of the excitation energy requires the inclusion of solvent. A spectrophotometric method for ascertaining the presence of anionic detergent in milk using azure A dye is described in literature [6]. In the previous research vibrational assignments for the observed Raman bands, based on the computed potential energy distribution (PED) and isotopic shifts were made [7]. First time, azure B has been used as achromogenic reagent for the spectrophotometric determination of product. The proposed method, which is simple and rapid, offers the advantages of sensitivity and wide range of determinations without the need for extraction or heating and it does not involve any stringent reaction conditions [8]. Excited electronic states of molecular systems can be calculated by TD DFT and TD HF methods [9–15].

Density functional theory is conceptually and computationally very similar to HF theory, but it provides vastly improved results and has outcome turned into an exceptionally prevalent technique. The aim of the current work is to study photophysical properties (photochromism, isomerization) and anisotropy of thermal conductivity in colored stretched PVA-films by *ab initio* (HF, DFT), UV/Vis- and IR-Spectroscopies and Indicator methods for determination of Thermal Conductivity of polymer films.

2. Experimental

2.1. Reagent and physical measurements

All chemical were used of analytical reagent grade. Used PVA «Mowiol 28–99» manufactured by the Hoëchst Com (Germany). Experimental UV–Vis spectrum of the compound was recorded on UV–Visible Spectrophotometer Cary 300 (Varian, USA). Experimental IR spectrum of films was recorded in the frequency region 400–4000 cm^{-1} on a spectrophotometer of Protégé 460 (Nicolet, US).

Photostability of films was studied using unfiltered radiation of high-pressure Hg-lamp DRSH-1000. The intensity of light falling perpendicular to the surface of the sample was 0.009 W/cm^2. At an exposure temperature of sample was 20–22 °C. The absorption spectra of the films were measured before and after radiation. Heat conductivity of films was measured on the complex equipment LC – 201 using indicator method of determining the heat conductivity of polymer materials.

2.2. Preparation

PVA films were prepared from 10% PVA solutions, containing the AZAC, gelling and plasticizing agents [16]. The films were cast on the polished glasses and dried in the closed box at temperature 20–22 °C. Uniaxial orientation was done in the 4% boric acid (H_3BO_3) solution at 42–45 °C. The washed film was dried for 30 min at temperature 60–63 °C. The value of stretching degree (R_s) was determined as the ratio between the length of the films after and before uniaxial stretching. The thickness of the resulting films was between 50 and 55 μm.

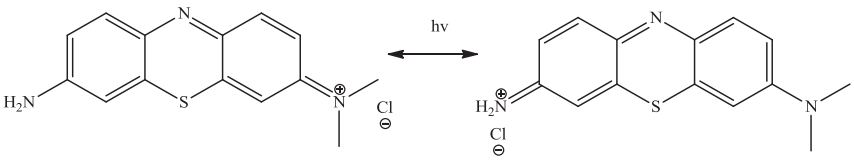
3. Computational details

The theoretical molecular structures of AZAC and AZAC1 in the ground state were optimized by HF/6-31G*, HF/6-311G* and DFT/B3LYP/6-311G* levels of theory in DMF and aqueous medium. Theoretical absorption spectra of the molecules optimized in solvents (DMF and water) were calculated using TDHF/6-31G*, TDHF/6-311G* and TDB3LYP/6-311G* methods. To account solvent effect Polarized Continuum Model (PCM) was used. The theoretical IR spectrum of optimized molecules was calculated using the DFT/B3LYP/6-311G* method. The scaling factor for the level of the theory is 0.98. The input files of both molecules were prepared by Gauss View and also used for the visualization of the structure and simulated vibrational and UV spectrum [17]. All the calculations are carried out using Gaussian 09 package [18].

4. Results and discussion

4.1. Geometric structure of AZAC and AZAC1

The geometry of the molecules AZAC and AZAC1 has been optimized using DFT/B3LYP/6-311G* levels of theory (Fig. 1). The calculated structural parameters bond lengths and bond angles of the molecules are presented in Tables S1& S2.



4.2. Electronic spectrum

Experimental and theoretical calculations demonstrate that AZAC molecule is very sensitive to the presence of solvents due to a total charge of its molecule, and it reacts with a solvent and change the absorption spectrum of AZAC. Calculated absorption spectra of AZAC in water, DMF and experimental spectra of AZAC in water are presented (Fig. 2). In the transition from water to DMF, absorption peak in the UV region does not undergo a large change, while in the visible region hypsochromic shift with absorption band occur at