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Effect of UV-irradiation on spectral properties of squaraine dye in diluted solutions

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ABSTRACT

The photosensitive symmetric derivative of quadratic acid (DMSAQ) was been synthesized for the biomedical or analytical purposes. The photochemical properties of the obtained dye were studied by means of absorption spectroscopy in six solvents of different polarity and photoreactivity: chloroform ($CHCl_3$), tetrahydrofuran (THF), ethanol (EtOH), acetonitrile (ACN) dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Both high-energy radiation (UV–vis) and radiation with lower energy from visible range were applied. It was found that the fastest squaraine dye bleaching takes place in $CHCl_3$ and DMF solutions, which is caused by photosensitivity of these solvents. The most spectacular stabilization effect has been found in DMSO under both visible and ultraviolet radiation. It was shown that the course of photochemical reactions of squaraine in solutions depends on the solvent properties, energy of radiation and mutual solute-solvent interactions. The explanation of squaraine structure and molecular interactions and their impact on photochemistry of studied systems has been supported by theoretical calculations.

1. Introduction

Squaric acid and its divalent anions, which have an aromatic character due to equally distributed charges between both oxygen atoms (contrary to an undissociated acid), are valuable starting materials for the preparation of compounds exhibiting photosensitivity.

Derivatives of squaric acid – squaraine dyes – due to their unique optical and biological properties as well as high stability, are useful in medical applications, for example, as inhibitors of protein tyrosine phosphatases or agents for photodynamic anticancer therapy [1–3]. Among other fields of squaraines usage, the technology of imaging and sensitizers for solar cells can be mentioned [4–6].

The recent contributions on this class of compounds have concerned the studies of their structure, intermolecular interactions, excited states and processes of electron transfer [7–9]. Many squaraine dyes exhibit the possibility of formation of dimers or larger aggregates [10]. Moreover, also the photochemical properties of squaraines were investigated in the 90s of the last century [11–15], however the available data are incomplete and do not concern the system analyzed in the present study.

The photochemical properties of this class of compounds depend not only on their chemical structure but also on the environment and conditions of experiments (solvent type, the presence of oxygen or photosensitive impurities). Additionally, the organic dyes are often used as photosensitizers in various chemical and biological reactions occurring also in nature, among which the photosensitized oxidation is of crucial importance.

Although various derivatives based on the squaric acid have been synthesized and characterized so far, there is still a need for new, more perfect compounds of this type with specifically tailored and controllable properties (including good solubility) that may be acquired in a simple, efficient and reproducible way. Furthermore, the detailed and systematic characteristics of their properties (photochemical among others) is necessary.

The aim of this work was to obtain a symmetric squaraine containing dimethylaminophenyl substituents, namely bis(4-dimethylaminophenyl) squaraine (DMASQ) and study its photochemical properties in different solvents providing relatively good solubility necessary for any further applications. In order to eliminate the formation of aggregates, the diluted solutions have been used. The introduction of amine groups into a dye is important for its usage in biomedical sectors since it increases the dye affinity to proteins and other bioactive compounds. The

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structure of the dye and the mechanism of its photolysis in various solvents have been explained in the present study on the basis of spectroscopic analysis and theoretical calculations, which allowed to investigate the molecular geometry, electron density and interactions between molecules.

The selection of solvent for photochemical studies is very important. The solvent should meet certain requirements, in particular, should not absorb in the same range as the test substance and do not react with it and its excited states. In our case, the number of non-reactive solvents has been limited because of the lack of solubility of the dye in some of them. Thus, tetrahydrofuran (THF), ethanol (EtOH), acetonitrile (ACN) dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were chosen for investigation. The effect of photoreactive solvents such as chloroform ($CHCl_3$) has been also studied for comparison. Solvent polarity strongly affects the charge transfer and the competing energy transfer, which are fundamental processes for photochemistry. The solvent choice is also important for physical processes such as crystallization, extraction, chromatographic separation of demanded compound [16].

2. Experimental

2.1. Materials

Reagents: squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) and *N,N*-dimethylaniline have been supplied by Aldrich.

All solvents: *n*-butanol, benzene, chloroform, ethanol, acetonitrile, tetrahydrofuran, *N,N* -dimethylformamide and dimethyl sulfoxide with a high degree of purity were also purchased from Aldrich and used without further purification.

2.2. Synthesis

Squaric acid (23 mg, 0.2 mmol) and *N,N*-dimethylaniline (59 mg, 0.48 mmol) were added to the 20 mL of mixture of solvents: *n*-butanol and benzene (v/v, 1:1) and striied at 120 °C with Dean-Stark trap for 24 h. The precipitated blue solid was separated by filtration and purified by crystallization from 1,2-dichloromethane/hexane solution (v/v, 4:1). Bis(4-dimethylaminophenyl) squaraine bluepowder was dried in vacuum to give a product with 59% yield (37.6 mg, mp: 294–296 °C).

2.3. Irradiation conditions

The solutions of squaraine dyes in all selected solvents (with a concentration of the order 10^{-5} M) were subjected to UV irradiation using polychromatic lamp (type HPK 125W, Philips, Holland), which emitted radiation in the range of 248–578 nm.

Both unfiltered radiation and filtered visible light (after UV cut-off by a glass filter) was used. The incident radiation intensity was measured by the IL 1400A Radiometer (International Light, USA). The intensity of total radiation (UV + Vis) and filtered Vis was equal 11.24 and 7.9 mW/cm^2, respectively.

2.4. Analysis

The UV–vis spectra of the dye solutions have been recorded using UV-1601 PC (Shimadzu, Japan) spectrophotometer in the 200–800 nm range after each irradiation period.

2.5. Theoretical calculations

The geometry optimization of the isolated DMASQ molecule was performed with PBE0-D3/cc-pVTZ approach. The nature of the obtained structure was confirmed by the harmonic vibration analysis. Additionally, the geometry of the ground state of DMASQ was optimized within the PCM model for the six analyzed solvents: $CHCl_3$, THF, EtOH, ACN, DMF and DMSO. The vertical excitation energies were estimated with the linear response formalism. In order to verify the correct description of the solvent effects by the PCM model, also the explicit complexes of DMASQ with the solvent molecules were investigated. The two sizes of the complexes were included into the considerations: with one solvent molecule and

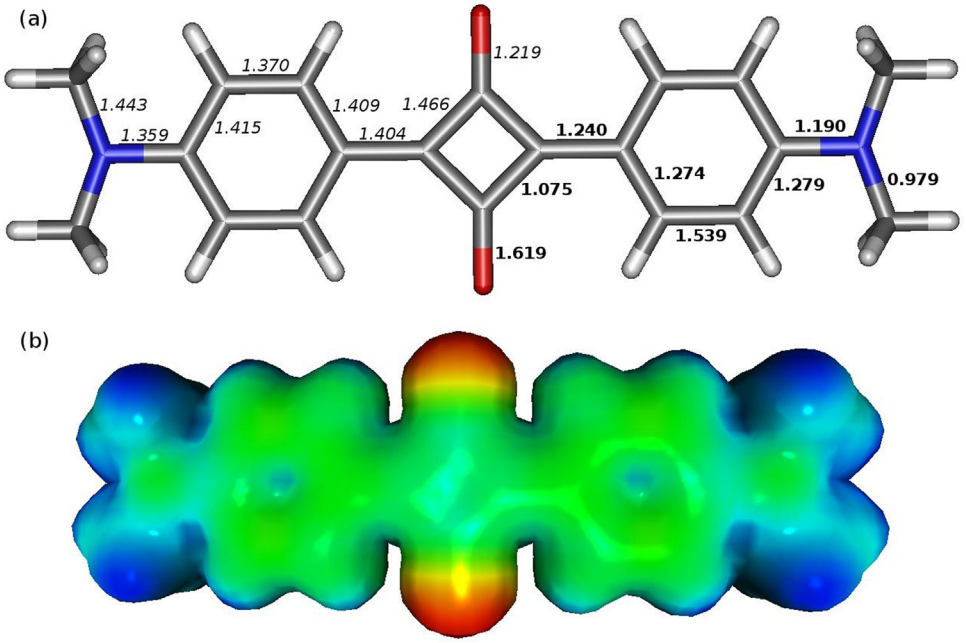

Fig. 1. PBE0-D3/cc-pVTZ optimized structure (D_{2h} symmetry) of DMASQ: (a) corresponding bond lengths (italic) and Wiberg bond orders (bold face) are given (the remaining numbers can be obtained by symmetry); (b) the DMASQ electrostatic potential (red color denote the negative potential and blue color-positive potential; color plot can be viewed on-line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)