Journal of Molecular Structure 1071 (2014) 133–138

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Spectroscopic study of photo and thermal destruction of riboflavin

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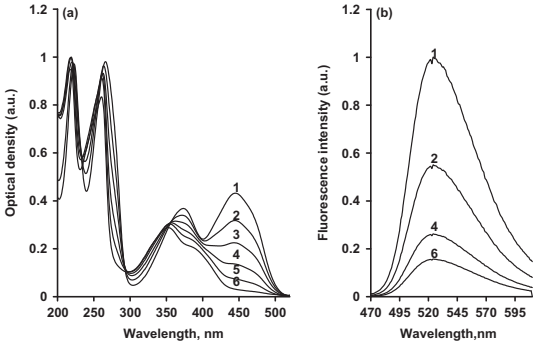
HIGHLIGHTS

- The influence of temperature and light irradiation of aqueous solutions riboflavin was studied.
- The riboflavin has undergone destruction depending on the concentration and magnitude of temperature effects.
- The presence of various acids and metal ions in the solution leads to increased photostability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 November 2013
Received in revised form 23 April 2014
Accepted 23 April 2014
Available online 2 May 2014

Keywords:
Riboflavin
Fluorescence
Thermal destruction
Linear dichroism
Photochemistry
Ion metals

ABSTRACT

Influence of temperature and light irradiation on the spectroscopic properties of aqueous solutions of riboflavin was studied using linear dichroism method, absorption and fluorescence spectroscopy. It was established that in a wide temperature range 290–423 K there is a decline of absorbance and fluorescence ability, which is explained by thermodestruction of riboflavin. It is shown that the proportion of molecules, which have undergone degradation, are in the range of 4–28%, and depends on the concentration and quantity of temperature effects. Introduction of hydrochloric and sulfuric acids, as well as different metal ions leads to an increase in the photostability of riboflavin solutions by 2–2.5 times. The observed phenomena are explained by the formation protonation form of riboflavin and a complex between the metal ions and oxygen atoms of the carbonyl group of riboflavin, respectively.

Introduction

Riboflavin is one of the most important water-soluble vitamins involved in many biochemical processes [1,2]. However, solutions of organic compounds are mostly used in practice; their molecules can be in a different molecular forms each characterized by own absorption and fluorescence spectra [3], as well as in multi-component mixtures where a variety of intermolecular interactions may affect the spectral–luminescence characteristics of organic compounds. Along with the spectral–luminescence characteristics of the solutions, an important parameter that determines the working resource is a photo and thermostability. Photophysical and photochemical processes occurring in solutions of riboflavin fairly well studied [4–7]. During the production of various riboflavin containing drugs they can be thermally treated for sterilization purposes, as a result significant changes of riboflavin properties may occur as a side effect. [8]. Therefore, the study of spectral-luminescent properties, photochemical degradation mechanisms, the influence of temperature and the development of non-chemical methods of stabilization of riboflavin is of great practical

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http://dx.doi.org/10.1016/j.molstruc.2014.04.077
0022-2860/

importance. That is why the purpose of present work is to study the effect of the concentration of riboflavin and various metal ions on the intermolecular interactions in solutions of riboflavin, as well as on their thermal and photo-stability.

Methods and experiment

Riboflavin powder with the "chemically pure" grade was used (Fig. 1). Distilled water was used as a solvent. Electronic absorption spectra were measured by a Specord 50 SA spectrophotometer (Analytikjena, Germany), with specified +/−0.003 D accuracy and 0.3 nm spectral resolution over the 190–1100 nm range.

Measurement of the fluorescence spectra was carried out by fluorescence setup, assembled on the base of two MDR-76 monochromators (LOMO, Russia). Photomultiplier tube FEU-38 (Russia) was used as detector. PMT signal was amplified and then registered by KSP-4 plotter. The angle between the excitation light and fluorescence observation was about 45°. To avoid reabsorption, fluorescence measurements were carried out with thin layers of the solutions, in which the absorption of the excitation light did not exceed ~5%. Depending on the concentration of the solution, special quartz cells with thickness of the layer in the range of 0.1–50 mm were used. In the case of absorption measurements, the cell thickness D and solution concentrations C were chosen so that C × D remains constant. In this case, despite the difference in the cell and concentration, the amount of absorbing molecules remains the same, allowing the direct quantitative comparison of spectrums. During irradiation by unfiltered light of a mercury-quartz lamp PRK-2 the distance between the lamp and the object was 15 cm, the irradiated area of the cell (diaphragm) 15.2 sm^2, optical power 60 mW. Riboflavin solutions were subjected to accelerated aging by heat treatment: for solutions by boiling under normal conditions and by keeping solutions in a thermostat at 343–423 K in tightly sealed cuvettes. A special hear-resistant capsule was used during the thermal treatment of aqueous solutions of riboflavin. In order to reduce the pressure of water vapor a cooling unit was mounted to the capsule: water vapor condensates in this unit and flows back to the heat-resistant capsule. Dispersion of optical rotation and linear dichroism spectra were recorded on a circular dichrographs Jasko-20, applying a double Fresnel parallelepiped specifically designed and fabricated for the visible and UV spectral region. For ease of comparison, the presented absorption and fluorescence spectra are normalized to unity. Calculation of charge distribution on the atoms was held during the quantum chemical calculations of molecular structure of riboflavin (Fig. 1) using the program package MOPAC 2009 [9] by semi-empirical method AM1 with a standard set of parameters [10]. All calculations were performed for isolated molecules in a vacuum. Prior geometry optimization of molecules was performed using a limited method Hartree–Fock with Polak–Ribiera algorithm up to 0.001 kcal/(Å × mol) and consideration of various options initial conformations.

Results and discussion

Influence of metal ions and the concentration

The concentration dependence of the absorption and fluorescence spectra of aqueous riboflavin solutions were studied (Fig. 2).

It can be seen from the Fig. 2 absorption and fluorescence spectra in the range 10^{-6}–10^{-5} M concentration remain constants. The absorption spectrum of riboflavin has four maximums with λ_{max} = 220 nm, λ_{max} = 265 nm, λ_{max} = 370 nm and λ_{max} = 440 nm. An aqueous solution of riboflavin has an intense fluorescence band with λ_{max} = 527 nm. A further increase in concentration leads to a decrease of the intensity and broadens the absorption spectra. Concentration increase in fluorescence spectra is manifested by the drop in the intensity, in other words, the concentration

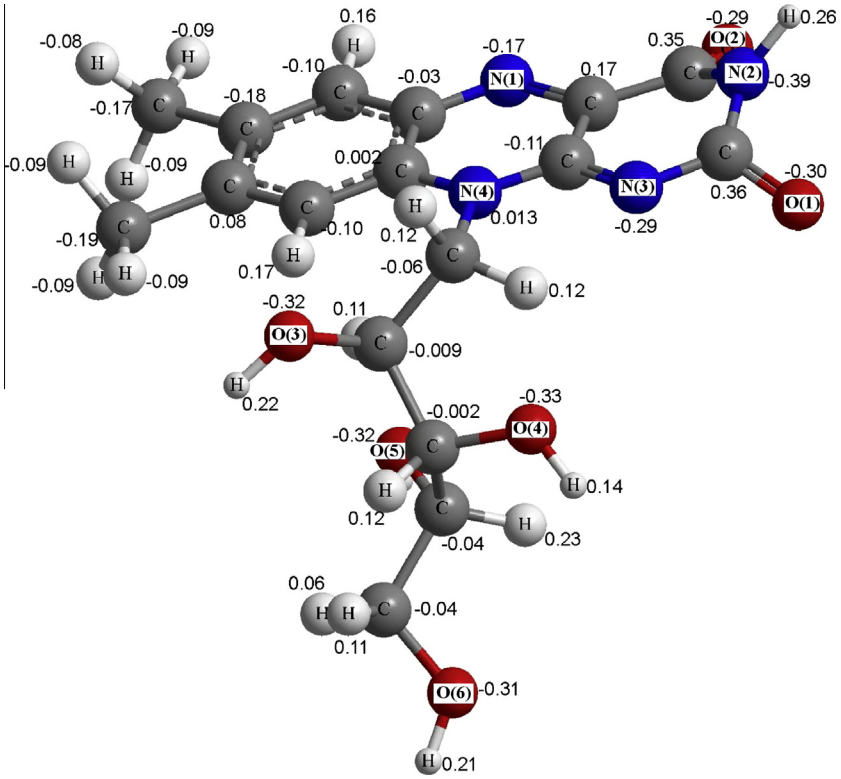

Fig. 1. Structural formula and the distribution of charges in the riboflavin.