

Electron structure and nature of electron transitions of squaraine and thiosquaraine as well as their 1,2-isomers



V.V. Kurdyukov^a, O.I. Tolmachev^a, O.D. Kachkovsky^a, E.L. Pavlenko^{b,*}, O.P. Dmytrenko^b, N.P. Kulish^b, R.S. Iakovyshen^b, V.A. Brusentsov^b, M. Seryk^b, A.I. Momot^b

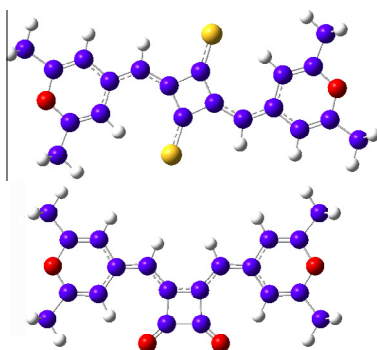
^a Institute of Organic Chemistry, National Academy of Sciences, Murmanskaya 5, Kiev 03094, Ukraine

^b Taras Shevchenko National University of Kyiv, Faculty of Physics, 64/13, Volodymyrska str., Kyiv 01601, Ukraine

HIGHLIGHTS

- We study squaraine and thiosquaraine with 2,6-di-*t*-Bu-substituted pyrylium residues and their 1,2-isomers.
- Both isomers exhibit similar electronic structures in ground state.
- UV–Vis absorption spectra of isomers differ due to the conjugated system.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 January 2014

Received in revised form 18 July 2014

Accepted 30 July 2014

Available online 8 August 2014

Keywords:

Squaraines

UV–Vis absorption

Quantum-chemical calculations

NMR spectroscopy

ABSTRACT

This paper presents the results of spectral measurements of UV–Vis absorption and ¹³C NMR spectra as well as quantum-chemical studies of molecular geometry and electron structure of squaraine, thiosquaraine and their corresponding 1,2-isomers. In the ground state 1,3- and 1,2-isomers have similar charge distributions and bond lengths within their chromophores but differ substantially in energy gap sizes and spectral properties, most prominently the maxima positions and intensities of long wavelength absorption bands. The replacement of oxygen atoms connected to the central cycle in squaraine with less electronegative sulfur atoms evokes a relatively intensive band in the short wavelength spectral region.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Cyanines are a special type of cationic polymethine dyes (PMDs). Along with their neutral derivatives and α,ω -disubstituted polyenes, they are well-known due to their strong selective absorption across a broad spectral region [1–4]. The main chromophore in cyanines consists of an extended chain of methine groups

(the polymethine chain) capped by two terminal groups with their own branched conjugated systems. Symmetrical PMDs were initially used as sensitizers of silver halides, laser media, fluorescence probes, etc., whereas asymmetrical cyanine dyes, including hemicyanines and merocyanines, have shown strong nonlinear optical properties (primarily large molecular hyperpolarizabilities), high transition moment and relatively low transition energy [1–6]. Terminal groups in such dyes can be composed from various heterocycles. One of the promising ways in the molecular design of new dyes with specified spectral characteristics is the introduction

* Corresponding author. Tel.: +380 44 526 05 02.

E-mail address: lenu4ka_pavl@mail.ru (E.L. Pavlenko).

of terminal residues with their own extended π -electron systems in order to increase the total length of conjugation [3,7].

Cyanine dyes with their simple chromophores are favored objects for testing new theoretical concepts, from the Hückel model [8–10] to the theory of solitonic charge waves [11–16]. One of the most important problems in the color theory of cyanine dyes is to investigate the dependency of charge distribution and electron transitions on the type of the linear conjugated system. In 1978 Daehne [17] introduced the concepts of the ideal polymethine and ideal polyene states, which differ fundamentally in the distribution of atomic charges and bond lengths. The ideal state in symmetrical polymethine dyes is achieved when electron densities at neighboring carbon atoms in the chain are alternated to the maximum extent and bond lengths are completely equalized. In this regard the ideal polyene state may be seen as diametrically opposite: the atomic charges are completely equalized and the lengths of neighboring C–C bonds are extremely alternated. Linear conjugated molecules can be generally viewed as intermediates between these two ideal types.

The features of electronic structure and the nature of electron transitions in different kinds of polymethine dye derivatives of squaric acid, the so-called squaraines or squaraine-cyanines, were investigated in detail [18–20]; it was established that squaraines exhibit electronic and spectral properties typical to polymethine. The point of interest is now to study an isomer of the squaric acid – the 1,2-analogue of a regular 1,3-squaraine and to compare the electronic structures and other properties of these two compounds. This paper concerns with squaraine isomers containing t-Bu-pyrylium residues as terminal groups and their thia-analogues, which absorb ultraviolet and visible light in a longer-wavelength spectral region.

Materials and methodology

The structural formulas of 1,3-squaraine (dye **1**), 1,3-thiosquaraine (dye **2**) and their corresponding 1,2-isomers (dyes **3** and **4**) are presented in Fig. 1. The synthesis of these molecules has been detailed in earlier papers [21,22].

Nuclear magnetic resonance spectra measurements were carried out on a Varian GEMINI 2000 spectrometer with ^1H and ^{13}C frequencies of 400.07 and 100.61 MHz respectively at 293 K. Tetramethylsilane was used as a standard for δ (NMR chemical shift) scale calibrating. ^1H NMR spectra were recorded with a spectral width of 8000 Hz (32,000 points); ^{13}C NMR spectra were recorded with a spectral width of 30,000 Hz (128,000). ^1H – ^{13}C COSY [23] spectra were acquired into a 2048 (F2) – 512 (F1) time-domain data matrix and a 2048 (F2) – 2048 (F1) frequency-domain matrix after zero-filling. NOESY [24] spectra were acquired, where necessary, with same parameters. Mixing times were pre-determined from T1-measurements for each sample with a conventional inversion-recovery method. Heteronuclear chemical shift correlation (HETCOR) was used to determine the ^1H – ^{13}C attachment using a

2048 (F2) – 256 (F1) time-domain matrix and a 2048 (F2) – 1024 (F1) frequency-domain matrix after zero-filling. The average value of the single-bond constant JCH was set to 140 Hz. The average value of the multi-bond C–H coupling constant was set to 8 Hz.

UV–Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in toluene, acetonitrile and ethylene glycol (spectral grade).

Quantum-chemical calculations were aimed at studying electronic structure and electron transitions under different molecular constitutions. Since only the π -system determines the essential properties of the molecules in question, the t-Bu substituents in pyrylium residues were replaced by methyl groups in the computational model. All calculations were performed in the Gaussian 03 software package [25]. Ground state equilibrium geometry optimizations were performed using the DFT/6-31G(d,p)/B3LYP model chemistry; electron transition characteristics were calculated using the non-empirical TD-DFT (6-31G(d,p)/B3LYP) and the semi-empirical ZINDO/S methods. There is typically no perfect coincidence of calculated and experimental data for this approach [26,27], however it is sufficiently accurate to correctly analyze the nature of electron transitions.

Results and discussion

Optimized molecular geometry

Isomeric derivative of squaric acid have notably different symmetries, namely the C_i symmetry in the 1,3-isomers (dyes **1** and **2**), and the C_{2v} symmetry in their 1,2-analogues (dyes **3** and **4**). The terminal 2,6-di-tert-butyl-pyrylium residues are symmetrical in respect to the axis drawn across the oxygen atom of the pyrylium cycle and the carbon atom that connects the residue to the external chain.

Optimized molecular geometries of different isomer models derived from dyes **1** and **3** are presented in Fig. 2. The lengths of carbon–carbon bonds within the models are given in Fig. 3. Calculations show that all four dyes are mostly planar, except for the model-specific methyl (tert-butyl in real molecules) substituents, which protrude from the molecular plane. Pyran cycles are almost planar in both molecules except for some deviations described in papers [21,22].

Carbon–carbon bond (C–C-bond) lengths can be separated into sets that belong to various molecular fragments: the terminal groups, the open chain and the central four-member cycle. Calculated C–C-bond lengths in the terminal heterocycle are seen from Fig. 3 to practically coincide in corresponding positions within all four dyes, i.e. regardless of the isomer type or the nature of the heteroatom in the central squaraine fragment (O or S): the difference between them is less than 0.01 Å. C–C-bond lengths in the 4-membered cycle of 1,3-squaraine (dye **1**) differ negligibly: their values are 1.482 and 1.475 Å, while in its thia-analogue (dye **2**) they are equal, each having a value of 1.466 Å. A larger difference is

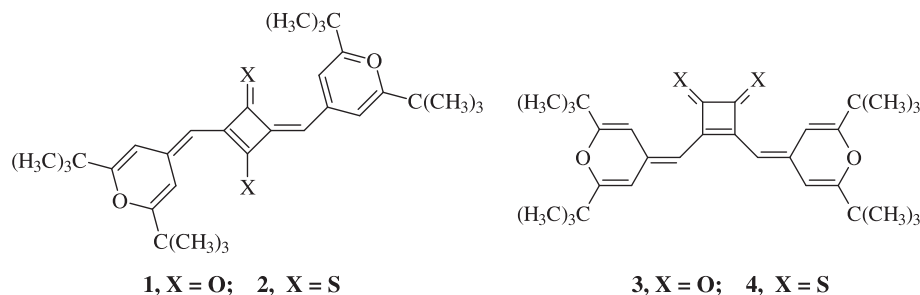


Fig. 1. Structural formulas of 1,3-squaraine (1), 1,3-thiosquaraine (2), 1,2-squaraine (3) and 1,2-thiosquaraine (4) with 2,6-di-t-Bu-substituted pyrylium residues.

Download English Version:

<https://daneshyari.com/en/article/1408493>

Download Persian Version:

<https://daneshyari.com/article/1408493>

[Daneshyari.com](https://daneshyari.com)