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Structural analysis of a dithiosquarylium dye

Sung-Hoon Kim [a, *], Sun-Kyung Han [a], Woo-Taik Lim [b], Nam-Ho Heo [b], Han-Chul Song [a]

[a] *Department of Dyeing and Finishing, Kyungpook National University, Taegu, 702–701, South Korea*
[b] *Department of Industrial Chemistry, Kyungpook National University, Taegu, 702–701, South Korea*

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Abstract

The MOPAC PM3 approach is used to study the structure of a dithiosquarylium dye (DTSQ). It was shown that the X-ray structure and the calculated results, are in good agreement. From the experimental and calculated structure of DTSQ, DTSQ-I is a more stables tructure than DTSQ-II. The structural analysis suggests that the DTSQ is extensively bond delocalized with relatively small torsion angles of 5°. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dithiosquarylium dye (DTSQ); MOPAC; Structural analysis; Solvatochromism

1. Introduction

Squarylium dyes form a class of dyes possessing intense absorption in the visible and near infrared regions [1]. Squarylium dyes and derivatives are 1,3-disubstituted compounds synthesized from squaric acid and two equivalent of various types of electron donating carbocycles and heterocycles [2–4]. The chemistry of squaric acid has been reviewed several times [5]. This class of cyanine dyes has attracted much attention because of their potential application in xerographic organic photoreceptors [6,7], optical recording media [8] and organic solar cells [9].

We have previously reported the synthesis [10], electroluminescence properties [11] and electrophotographic properties [10] of dithlosquarylium dyes (DTSQ). As in a previous paper [12] single crystal X-ray crystallography and crystal packing examinations have been employed to determine both the structure and the important intermolecular interactions in the solid state of DTSQ.

In this work the structure of DTSQ has been solved using MOPAC PM3 semi-empirical molecular orbital calculations in combination with X-ray structure data.

2. Results and discussion

2.1. Comparison between experimental and MOPAC PM3 geometry

An understanding of the relationship between the structure and properties of organic materials is crucial if they are to be designed and used for specific applications. Unfortunately, in general, organic dyes do not readily provide single crystals for X-ray structure determinations, which has

* Corresponding author. Tel.: +82-53-950-5641; fax: +82-53-950-6617; e-mail: shokim@bh.kyungpook.ac.kr

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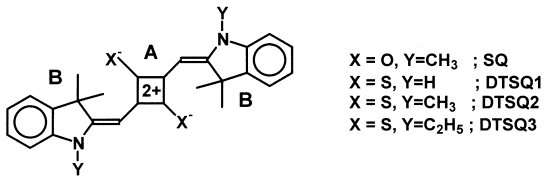
severely limited the data available for structure-characteristics study. Prior to this work there were two previously known crystallographic structures of squarylium dyes, SO and DTSQ, containing an indoline moiety [11,13].



From the X-ray structure, we can conclude that the molecules adopt the *trans* conformation. According to the results of an X-ray structural study of DTSQ, however, DTSQ is slightly twisted. The A ring is at an angle of 5.0° (±0.8) with respect to the B ring (Fig. 1).

The PM3 optimized bond lengths and experimental data are shown in Fig. 2. The values in Fig. 2 indicate that for the DTSQ the agreement between X-ray and PM3 bond lengths is very satisfactory. A considerable amount of double bond character in bonds 3 and 5 evidently exists between all conjugated systems.

A typical characteristic of such of a polymethine type formulation is the relatively even bond lengths between conjugated carbons. Thus, the average bond length should be between that of a single bonded C–C and a double bonded C=C. Even though DTSQ has two possible *trans* conformations, DTSQ-I and DTSQ-II, it seems that the most

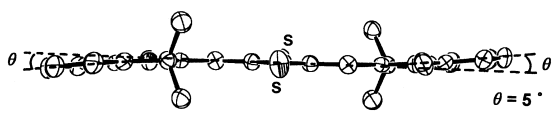


Fig. 1. Side view of DTSQ.

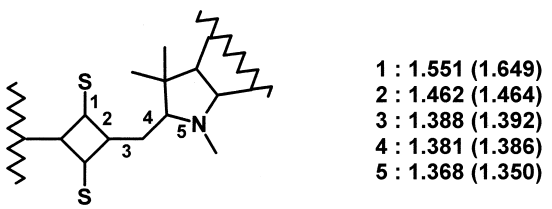


Fig. 2. Calculated bond lengths (Å) of DTSQ with experimental data in parentheses.

likely form which exists is the DTSQ-II form, due to steric hindrance of the geminal dimethyl groups around the dithiosquarate sulfur atoms. The most stable conformations and the heats of formations of DTSQ-I and DTSO-II were optimized using MOPAC PM3, and the results are shown in Fig. 3.

The heats of formation obtained show that in the gas phase, the DTSQ-I form is the more stable, in accordance with the experimental results for solid phase data. The resulting structure for DTSQ-II was found to be higher in energy by 12 kcal mol^{-1} (187.47 kcal mol^{-1} and 199.47 kcal mol^{-1} for DTSQ-I and DTSQ-II, respectively) than DTSQ-II. The calculated heats of formations were plotted against the dihedral angle between the four-membered ring A and the indolenine moiety B (Fig. 3). The most stable conformer was observed at 0° in both cases. The interatomic distance between the sulfur atom and the neighboring hydrogen atom is slightly longer (~0.3 Å) in DTSQ-II compared with that of DTSQ-I (2.08 Å in DTSQ-I, 2.34 Å in DTSQ-II) (Fig. 3). From the calculated results of the interatomic distance S...H and heats of formation, the conformation of DTSQ-I is energetically preferred to DTSQ-II because of steric hindrance factors.

2.2. Inverted solvatochromism of DTSQ

If the dye molecules possess a strong dipole, a polar solvent lowers the energy of the ground state more than that of the excited state, and the solvent thus produces a hypsochromic shift (negative solvatochromism [14].

Dimroth et al. have suggested that the transition energy for pyridinium-N-phenoxide betain dye, expressed in kcal mol^{-1}, be used as a polarity parameter [14]. This quantity is referred to as the E_T value. Solvatochomism studies were performed on DTSQ and SQ. Reasonable linear plots were obtained on plotting λ_{max} of SQ versus solvent parameter E_T (Fig. 4). As the solvent polarity increased, a hypsochromic shift was observed (i.e. negative solvatochromism).

On the other hand, DTSQ exhibits a hypsochromic and then bathochromic shift of λ_{max} as the solvent polarity increases. This surprising inverted solvatochromism indicates that the ground-state

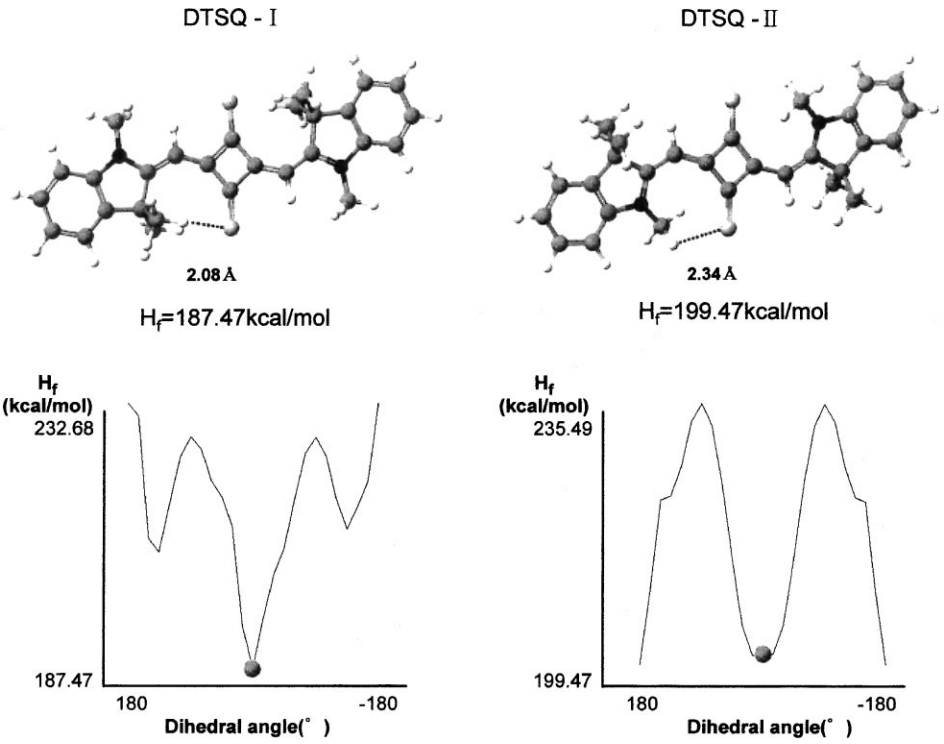


Fig. 3. The calculated energy profile of DTSQ-I and DTSQ-II by MOPAC PM3.

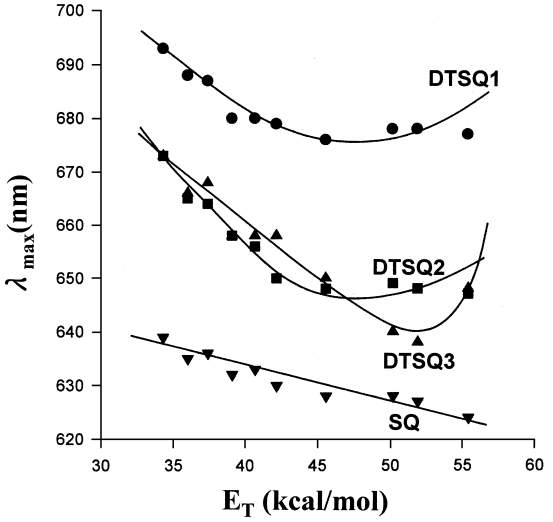


Fig. 4. Plots of λ_{max} vs E_T values for DTSQ ans SQ dye.

electronic structure of DTSQ changes with increasing solvent polarity, from $\mu_g > \mu_e$ to $\mu_g < \mu_e$ (where μ_g and μ_e are the dipole moments of the ground and excited states, respectively).

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