Journal of Photochemistry and Photobiology A: Chemistry 199 (2008) 23–33

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Study of the spectroscopic properties and first hyperpolarizabilities of disperse azo dyes derived from 2-amino-5-nitrothiazole

Antonio E.H. Machado[a,*], Newton M.B. Neto[b], Leonardo T. Ueno[a], Lucas F. de Paula[a], Diesley M.S. Araújo[a], Guedmiller S. Oliveira[a], Weverson R. Gomes[a], Rodrigo de Paula[a], Paulo L. Franzen[c], Sérgio C. Zilio[c], Ana M.F. Oliveira-Campos[d], A.M. Fonseca[d], Lígia M. Rodrigues[d], P.O. Nkeonye[d], Radim Hrdina[e]

[a] *Universidade Federal de Uberlândia, Instituto de Química, Laboratório de Fotoquímica, P.O. Box 593, Uberlândia, 38400-902 Minas Gerais, Brazil*
[b] *Instituto de Física, Universidade Federal de Uberlândia, Uberlândia, Minas Gerais, Brazil*
[c] *Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, São Paulo, Brazil*
[d] *Centro de Química, Universidade do Minho, Campus de Gualtar, Braga, Portugal*
[e] *Department of Organic Technology, Faculty of Chemical Technology, University of Pardubice, Czech Republic*

ARTICLE INFO

Article history:
Received 5 December 2007
Received in revised form 12 April 2008
Accepted 20 April 2008
Available online 29 April 2008

Keywords:
Azo dyes
Solvatochromism
EDA complexes
Fluorescence
Quantum mechanical calculations
First hyperpolarizability

ABSTRACT

The solvatochromism and other spectroscopic and photophysical characteristics of four azo disperse dyes, derived from 2-amino-5-nitrothiazole, were evaluated and interpreted with the aid of experimental data and quantum mechanical calculations. For the non-substituted compound two conformers, **E** and **Z**, were proposed for the isolated molecules, being the second one considerably less stable. The optimization of these structures in combination with a SCRF methodology (IEFPCM, simulating the molecules in a continuum dielectric with characteristics of methanol), suggests that the **Z** form is not stable in solution. This same behaviour is expected for the substituted compounds, which is corroborated by experimental data presented in previous investigations [A.E.H. Machado, L.M. Rodrigues, S. Gupta, A.M.F. Oliveira-Campos, A.M.S. Silva, J. Mol. Struct. 738 (2005) 239–245]. For the substituted compounds, two forms derived from **E** conformer (**A** and **B**) are possible. Quantum mechanical data suggest for the isolated molecules, that the low energy absorption band of the **E** conformers involve at least two close electronic states, having the low-lying excited state a $^1(n,\pi^*)$ nature, and being the S_2 state attributed to a $^1(\pi,\pi^*)$ transition. The data also suggest a small energy gap between the absorption peaks of **A** and **B**, related to the easy conversion between these forms. For the structures optimized in combination with the applied SCRF methodology, an states inversion is observed for the substituted compounds, with a considerable diminish of the energy gap between **A** and **B** absorption peaks. The electronic spectra of these compounds are quite sensitive to changes in the solvent polarity. The positive solvatochromism is more evident in aprotic solvents, probably due to the polarization induced by the solute. These compounds do not fluoresce at 298 K, but present a small but perceptible fluorescence at 77 K, which seems to be favoured by the nature of the group in the 2′-position of the phenyl ring. Moreover, such compounds present expressive values for first hyperpolarizability, which implies in good non-linear optics (NLO) responses and photoswitching capability.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Progress in areas such as optical communication, optical computing, dynamic image processing, and data storage, would be greatly enhanced by the availability of materials with sufficiently large non-linear optics (NLO) responses combined with other desirable properties, such as photoswitching. In view of this, extensive research efforts have been directed towards the preparation of more efficient photon-manipulating materials [1–5].

It is known that organic molecules formed by a donor–acceptor pair connected to a π-delocalized framework present attractive NLO characteristics, which can be estimated from their hyperpolarizabilities [1,5,6]. The first hyperpolarizability, for example, gives information about the material capability to generate second order non-linear effects, such as: second harmonic generation, sum of frequency, parametric amplification and others [6].

Azo dyes are of particular interest since they can be readily prepared with a wide range of donor and acceptor groups. Besides, the

* Corresponding author. Tel.: +55 34 3239 4428; fax: +55 34 3239 4208.
E-mail address: aeduardo@ufu.br (A.E.H. Machado).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.04.012

usually good planarity of the azo bridge which should contribute to larger π electron transmission effects [7–10]. In particular, azobenzenes, besides NLO properties, tend to exhibit photoswitching properties due to photo-induced *cis–trans* isomerization, making them promising for several technological applications [9].

Colour chemistry studies have demonstrated that the replacement of a benzene ring by a less aromatic heterocycle in typical donor–acceptor chromogens, such as azo and stilbene dyes, results in significant bathochromic shift of the visible absorption spectra [5,11,12], evidencing the enhancement of molecular hyperpolarizability [5]. Chippendale and co-workers described polymorphism for Disperse Red 278 due to slow exchange between two conformers [13]. Following the preparation of dyes **1**–**4** [14], a detailed investigation of dye **3**, by NMR, allowed us to assume that two forms were present (**A** and **B** conformers) in deuterochloroform solution and in the solid state, coexisting in equilibrium in an approximately 1:1 ratio at room temperature [15]. Besides, the polymorphism involving the *trans* form, *cis–trans* isomerization should also be considered. The understanding of how these phenomena correlate is one of the objectives of this paper.

In the present work, spectroscopic, photophysical and theoretical data were used to characterize the compound 2-(4′-*N*,*N*-diethylaminophenyldiazenyl)-5-nitrothiazole (compound **1**) and three acylamino derivatives of this dye (Fig. 1), and evaluate their solvatochromism and second order NLO capability. The synthesis and characterization of these compounds were previously reported [14].

2. Experimental

2.1. Spectroscopic measurements

UV/vis absorption, excitation and emission spectra were recorded using, respectively, a Shimadzu UV-2501 PC spectrophotometer and a HITACHI F-4500 spectrofluorimeter equipped with low temperature measurements accessories. The fluorescence spectra were obtained using the right angle configuration. For all experiments, the concentration of the solutions was between 2 and 3×10^{-6} mol dm^{-3}.

Fluorescence measurements were done at 298 and 77 K for solutions prepared in anhydrous ethanol. Fluorescence quantum yields were estimated from the corrected fluorescence spectra of the emission band with a maximum around 618 nm, using the secondary standard method. A methanol solution of cresyl violet ($\Phi_F = 0.54 \pm 0.03$; $\lambda_{exc} = 580$ nm) was used as fluorescence standard [16]. For these measurements, all solutions were prepared to present absorbance lower than 0.100 at the excitation wavelength to avoid light reabsorption effects. In the low temperature measurements, argon was used to deoxygenate the solutions. The xenon lamp was operated at 950 V, with the scanning rate adjusted at 240 nm min^{-1}. The emission and excitation slits were fixed at 2.5 mm.

All solvents (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 1-octanol, water, ethylene-glycol, *n*-hexane, chloroform, carbon tetrachloride, dimethylsulfoxide and acetone) were analytically pure or spectroscopic grade and were used as received.

2.2. Quantum chemical calculations

The molecular structure of these compounds was previously assessed using the PM3 semi-empirical method [17,18]. Afterwards, the optimization was refined using a Density Functional Theory (DFT) procedure based on the hybrid functional B3LYP, using the 6-31g(d,p) atomic basis set [19], from which the dipole moments and total energy of each system studied were estimated. These calculations were performed using the Gaussian 03W package [20,21]. The Berny analytical gradient was used in all DFT optimizations. The requested convergence limit on root mean square (RMS) density matrix was 1×10^{-8} and the threshold values for the maximum force and the maximum displacement were 0.000450 and 0.001800 a.u., respectively. Additionally, optimizations using a Self-Consistent Reaction Field (SCRF) methodology based on the IEFPCM (Integral Equation Formalism of Polarized Continuum Solvation Method) model [20] were done, defining methanol as solvent, to evaluate the influence of the solvent on the studied parameters. The 6-31g(d) atomic basis set was applied for this case.

The optimized structures (isolated molecules and the ones obtained by the application of the SCRF methodology) were used to estimate the components of the hyperpolarizability tensor [22], obtained by single point calculations using the PM3 semi-empirical method [18,23]. Application of these parameters in the following equation:

$$\langle\beta\rangle = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (1)$$

permitted to estimate the average value of the first hyperpolarizability, $\langle\beta\rangle$. The values of $\langle\beta\rangle$ are expressed in electrostatic units (1 a.u. = 8.6393×10^{-33} cm^5 esu^{-1}).

The excitation energies and oscillator strengths for the first 15 states of each of the studied compounds, were computed by TD-DFT calculations [24,25] using the 6-31g(d) atomic basis set. For the optimized structures based on the IEFPCM SCRF procedure, the TD-DFT calculations were done considering the structures previously optimized using the same SCRF methodology.

The state energies of the relaxed structures of compound **1** in the S_1 and S_2 states, optimized using the SCRF methodology combined with the Configuration Interaction Singles (CIS) approach [20] and the less expensive 3-21g* atomic basis set [26], were obtained by TD-DFT calculations based on the B3LYP hybrid functional and the 6-31G(d) atomic basis set. For these structures and for the S_0 state, the bond orders of some bonds were estimated using single point calculations based on the PM3 semi-empirical method [18].

Fig. 2 presents the **E**(**A**) conformation of compound **3**. The numbered atoms correspond to the geometric parameters used during the discussion. A representation of the **E**(**B**) conformation of this compound can be found in Ref. [15].

2.3. First hyperpolarizability measurements

The first hyperpolarizability ($\beta_{TOT} = \beta_{HRS}$) was measured using an extension of the conventional Hyper-Rayleigh Scattering technique (HRS) [27], named pulse trains hyper-Rayleigh Scattering (PTHRS). This technique allows improved and fast measurements, since mechanical movements, which could vary the intensity, are eliminated and higher frequency rates can be applied to acquire a large body of statistical data in a short time.

The samples were pumped by pulse trains composed by approximately 20 pulses of 70 ps separated by 13 ns, delivered by a Q-switched and mode-locked Nd:YAG laser at 1064 nm. As the complete Q-switch pulse train was used to pump the samples, each measurement involved more than ten different intensities of mode-lock pulses. To avoid noise and other than hyper-Rayleigh contributions (e.g. solvent ionization) the maximum intensity was left at the threshold of solution ionization, using for this purpose two crossed polarizers to limit the laser intensity. Moreover, any signal coming from another kind of process (e.g. two-photon fluorescence) would have to fall within the 3 ns response time of the

Download English Version:

https://daneshyari.com/en/article/27936

Download Persian Version:

https://daneshyari.com/article/27936

Daneshyari.com