



## A novel barbituric acid-based azo dye and its derived polyamides: Synthesis, spectroscopic investigation and computational calculations

Mohammad Reza Zamanloo\*, Amir nasser Shamkhali, Masoumeh Alizadeh, Yagoub Mansoori, Golamhassan Imanzadeh

Department of Applied Chemistry, Faculty of Basic Science, University of Mohaghegh Ardabili, Ardabil, Iran

### ARTICLE INFO

#### Article history:

Received 6 November 2011  
Received in revised form  
6 May 2012  
Accepted 14 May 2012  
Available online 2 July 2012

#### Keywords:

Azo dye  
Barbituric acid  
Computational calculations  
Tautomerism  
Polyamides  
UV–vis spectroscopy

### ABSTRACT

5-[(3,5-dicarboxyphenyl)azo]-barbituric acid, an azo-based aromatic diacid was prepared and fully characterized by FT IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR along with UV–vis absorption spectroscopy. The effects of varying pH and solvent upon the absorption spectrum of the azo dye were investigated. The optimized molecular structures of possible tautomeric forms and HOMO–LUMO energies of expecting preferred forms of the synthesized heterocyclic azo dye have been calculated using density functional theory, (B3LYP) methods with TZVP basis set level and Polarizable Continuum Model (PCM) model for solvation effect. The calculations showed that the most probably preferred form of the azo dye in gas phase and solution was a hydrazone-keto form. FT IR and UV–vis spectroscopy, DSC, TGA and XRD techniques were used to obtain the characteristics and structural features of the monomer-synthesized polyamides. The influence of organic solvents on the absorption spectra of the polymers along with viscosity measurements (0.19–0.44 dl/g), solubility and film formability of the synthesized polyamides were also investigated.

© 2012 Elsevier Ltd. All rights reserved.

### 1. Introduction

Azo dyes derived from heterocyclic systems exhibit modified dyeing and optical properties relative to the azo benzenoid compounds. The subject is clarified in higher sensitivity of their absorption spectroscopic properties to structural changes. Direct influence of heteroatoms on the molecular orbitals, low aromaticity and hyperpolarizability along with dependence of energy levels to substituent groups are the most important characteristics of heterocyclic compounds to access the diversity of optical absorption properties. Bathochromic shift in the absorption spectra of hetarylazo dyes is the most important features of their optical properties [1–7]. Azo dyes derived from various heterocyclic coupling components such as thiazole, thiophene and pyrazole are the instances of desired materials [8–15]. On the other hand, the possibility of tautomerism in hetarylazo compounds which induce light fastness and moreover coordination ability to metal cations to forming complexes can verify their application fields. It is well known that azo dyes with heterocyclic components exhibit good

tinctorial strength and brighter dyeing than those derived from benzenoids [16–19].

Azobarbituric acid derivatives are another class of hetarylazo compounds that characterize to show various tautomeric structures in their free acid form. They have versatile utilities as their salts, metal complexes, solid solutions, inclusion and intercalation compounds [20,21]. These organic pigments are distinguished by high tinctorial strength, great hiding power, very good light fastness properties, and excellent solvent fastness properties as well as heat resistance which all indebted to more tautomeric structures. Hence, they are applied as pigments in printing inks, distempers or emulsion paints. Some of the spectroscopic properties and tautomeric forms of azobarbituric acid derivatives have been described in recent publications [22–25].

Technical applications of azo-dye compounds mainly depend on the oxidative, thermal and solvent resistance, along with lightness strength and optical properties of the azo chromophore. More superior properties can be offered in the polymeric form in view of higher processability, free-standing film formability and photoactivity [26,27]. Three main procedures have developed to introduce an azo chromophore into a polymeric structure, including: blending of the organic molecular pigment with the polymeric matrix, chemical bonding of the pigment to the polymer structure and polymerizing the pigment-containing monomers resulted to

\* Corresponding author. Tel.: +98 4515514702; fax: +98 4515514701.

E-mail addresses: [zamanlou@yahoo.com](mailto:zamanlou@yahoo.com), [mrzamanloo@uma.ac.ir](mailto:mrzamanloo@uma.ac.ir) (M.R. Zamanloo).

the polymers with the chromophore in side chains or in the main chain. Non-leaching behavior combined with uniform dispersion of colorants in polymer matrix without aggregation is the major advantage of the last method. Hence, the design and synthesis of functional colorants with polymerization ability have received considerable attention [28–35]. Polyamides, as the most applicable engineering plastics, are of great importance in this regard for their applications as self-coloured materials. Their usages as fiber form in man-made textiles take a special attention because of the requirement to stability and improved thermal properties especially at colored state [36–40].

According to our literature survey there are a few publications on barbituric acid-based azo dye polymers and their metal complexes. In this research, a new azo dye monomer was synthesized from barbituric acid and utilized to prepare a series of aromatic polyamides. The optimized molecular geometries of seven tautomeric forms of the synthesized hetarylazo monomer were calculated to distinguish the most stable configuration playing an important contribution in controlling spectroscopic properties. The monomer and polymers with the chromophore in side chains were evaluated for absorption spectroscopic aspects in aqueous and organic media using UV–vis measurements.

## 2. Experimental

### 2.1. Materials

The used chemicals were purchased from Merck Chemical Co., Fluka Chemical Co., and Aldrich Chemical Co. 5-aminoisophthalic acid was recrystallized from a mixture of *N,N*'-dimethylformamide (DMF)/water (3/1 V). 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenylmethane and 1,5-diaminonaphthalene were recrystallized from ethanol/water (3/1 V). 1,4-diphenylenediamine, 1,3-diphenylenediamine and 4-methyl-1,3-phenylenediamine were sublimed under reduced pressure. *N,N*'-dimethylacetamide (DMAC), *N*-methyl pyrrolidone (NMP) and pyridine were stirred over powdered calcium hydride or KOH overnight and then distilled under reduced pressure. Triphenylphosphite (TPP) was used without further purification. Anhydrous calcium chloride was dried under vacuum at 120 °C for 5 h.

### 2.2. Instruments and measurements

Melting points were determined on a Stuart SMP-3 melting point apparatus with a heating rate of 2 °C/min and not corrected. Fourier transform infrared (FT IR) spectra (in KBr pellets) were recorded on a perkin-Elmer RX-1 spectrometer in the region of 4000–400 cm<sup>-1</sup>. Vibration transition frequencies are reported in wave-number (cm<sup>-1</sup>). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 MHz and 75 MHz spectrometer respectively, in DMSO-d<sub>6</sub> using tetramethylsilane (TMS) as an internal reference. Multiplicity of proton resonances was designated as singlet (s), broad (br) and multiplet (m). A double beam shimadzu UV-1650 PC spectrophotometer was used to record the absorption spectra over a wavelength range of 200–600 nm. Quartz cuvettes were used for measurements in solution. The diffuse reflectance spectra were recorded on powder samples with a Color GrapG™ spectrophotometer (Miton Roy Co). Differential Scanning Calorimetry (DSC) was done using an NETSCH DSC 200 F3. The measurements were performed in the range of 25–400 °C at a heating rate of 10 °C/min under a nitrogen atmosphere as cycles consisting of 1st heating–cooling–2nd heating scans. Glass transition temperatures (*T*<sub>g</sub>) were read at the middle of inflections in

DSC traces. Thermogravimetric analysis (TGA) was performed with a PL 1500-TGA at a heating rate of 10 °C/min under nitrogen atmosphere. Inherent viscosities ( $\eta_{inh}$ ) were obtained on 0.5% (w/v) polyamide solutions in H<sub>2</sub>SO<sub>4</sub> at 30 °C by an Ostwald Routine Viscometer (Germany). Wide-angle x-ray diffraction (XRD) measurements were performed at room temperature on a Siemens D500 x-ray diffractometer (Germany) using Ni-filtered Co–K $\alpha$  radiation.

### 2.3. Synthesis

#### 2.3.1. 5-[(3,5-dicarboxyphenyl)azo]-barbituric acid (monomer) (IV)

5-aminoisophthalic acid (1.00 g, 5.52 mmol) was dissolved in 12.0 ml of a mixture of DMF and concentrated hydrochloric acid, (2/1 V). The solution was then cooled to –5–0 °C and sodium nitrite (0.427 g, 6.18 mmol, 14.2% aq) was added dropwise with vigorous stirring. The resultant mixture was stirred for 30 min at 0 °C, and then 0.707 g (5.52 mmol) of barbituric acid dissolved in 5 ml of aqueous solution of sodium acetate 5% (w/v) was added portionwise to the diazonium solution. The resulting mixture was stirred for 3.5 h at that temperature. A yellow solid product separated upon dilution with cold water which was filtered off and washed several times to reach neutral state. The crude dye was purified by reprecipitating of DMF solution to a large amount of water to afford a bright yellow powder (1.66 g, 94%, vacuum dried at 100 °C for 3 h). d.t. 319–326 °C, FT IR(KBr, cm<sup>-1</sup>): 3450 (m), 3200 (m), 3079 (m), 2848 (w), 1720 (s), 1670 (s), 1643 (m), 1527 (s), 1458 (s), 1434 (s), 1397 (s), 1278 (s), 1218 (s), 1085 (w). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm): 8.25 (s, 2H), 8.34 (m, 1H), 11.34 (s, 1H), 11.53 (s, br, 1H), 14.06 (s, br, 1H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm): 166.5 (C<sub>11, 12</sub>), 162.1 (C<sub>4</sub>), 160.2 (C<sub>2</sub>), 150.2 (C<sub>1</sub>), 142.9 (C<sub>6, 10</sub>), 133.1 (C<sub>8</sub>), 126.9 (C<sub>7, 9</sub>), 121.7 (C<sub>5</sub>), 119.4 (C<sub>3</sub>). Elemental analysis calculated for C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>O<sub>7</sub>: C, 45.00%; H, 2.52%; N, 17.50%; Found: C, 44.12%; H, 3.20%; N, 16.95%.

#### 2.3.2. Synthesis of model compound

In a 50 ml round-bottom flask equipped with a magnetic stirrer and reflux condenser, were placed 0.500 g (1.56 mmol) of dicarboxylic acid (IV), 0.335 g (3.12 mmol) of *p*-toluidine, 1.938 g (6.24 mmol, 1.64 ml) of TPP, 4.0 ml of DMAC, 0.8 ml of pyridine and 0.78 g of CaCl<sub>2</sub>. The mixture was heated with stirring at 110 °C for 6 h under argon atmosphere. After cooling, 100 ml of methanol was poured into the resulting mixture and the yellowish precipitate was filtered off, washed thoroughly with methanol and dried in vacuum at 100 °C for 4 h. The purification of the product was performed by reprecipitating from DMF to methanol (0.51 g, 65.4%), d.t. 335–341 °C. FT IR (KBr, cm<sup>-1</sup>): 3425 (s), 3133 (m), 3067 (m), 2920 (m), 2852 (m), 1741 (s), 1722 (s), 1665 (s), 1650 (s), 1597 (s), 1533 (s), 1518 (m), 1451 (w), 1420 (m) 1395 (s), 1317 (s), 1279 (m). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm): 2.28 (s, 6H), 7.17 (d, *J* = 7.2 Hz, 4H), 7.67 (d, *J* = 7.2 Hz, 4H), 8.25 (m, 2H), 8.32 (s, 1H), 10.42 (t, *J* = 14.8 Hz, 2H), 10.88 (s, 1H), 11.39 (s, br, 1H), 14.23 (s, br, 1H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm): 165.3 (C<sub>11</sub>), 164.7 (C<sub>4</sub>), 150.2 (C<sub>2</sub>), 142.3 (C<sub>1</sub>), 137.2 (C<sub>7, 9</sub>), 137.0 (C<sub>15</sub>), 133.4 (C<sub>12</sub>), 133.37 (C<sub>6, 10</sub>), 129.5 (C<sub>14, 16</sub>), 124.0 (C<sub>5</sub>), 120.9 (C<sub>8</sub>), 119.4 (C<sub>13, 17</sub>), 118.8 (C<sub>3</sub>), 21.0 (C<sub>18</sub>) ppm.

#### 2.3.3. Synthesis of polyamides (PAa-h)

The phosphorylation polycondensation method was used to prepare the polyamides. As a typical case: In a 50 ml round-bottom flask equipped with a magnetic stirrer and reflux condenser, were placed 0.500 g (1.56 mmol) of dicarboxylic acid (IV), 0.308 g (1.56 mmol) of 4,4'-diamino diphenyl methane, 1.938 g (6.2 mmol, 1.64 ml) of TPP, 5.0 ml of DMAC, 0.50 ml of pyridine and 0.780 g of CaCl<sub>2</sub>. The reaction mixture was heated with stirring at 120 °C for 8 h under argon atmosphere. As the polycondensation proceeded, the solution gradually became viscous. After cooling, 100 ml of

Download English Version:

<https://daneshyari.com/en/article/176840>

Download Persian Version:

<https://daneshyari.com/article/176840>

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