A combined experimental and TD-DFT investigation of three disperse azo dyes having the nitroterephthalate skeleton

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ABSTRACT

Three disperse azo dyes were synthesized using diazotized dimethyl 2-amino-5-nitroterephthalate **(5)** followed by the diazo coupling with different N-substituted aromatic amines. The structures of the dyes were confirmed using FT-IR, ^{1}H NMR, ^{13}C NMR, MS and HRMS spectral analysis. The geometries of the azo and hydrazone tautomeric forms of the dyes were optimized at B3LYP/6-31G(d) level of theory, and their electronic excitation properties were evaluated using density functional theory. The computed absorption spectral data of the azo derivatives are in good agreement with the experiment, thus allowing an assignment of the UV–vis spectra. The dyes displayed a broad absorption maximum in the visible region between 498 and 561 nm. The synthesized azo disperse dyes were applied on polyester and nylon fiber and they show very good light fastness and washing fastness properties.

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1. Introduction

Azobenzenes have versatile applicability ranging from textile dyeing [1], leather dyeing [2], coloring of plastics and polymer [3] to advanced applications such as liquid crystal displays [4], biological and medical studies [5]. In addition to the above features, azobenzenes have interesting properties like the reversible *cis-trans* photoisomerization about the azo π-bond when heated or irradiated in UV [6]. Also, they contribute to the greatest production volume of the dyestuff industry due to simplistic mode of their synthesis with a high atom economy.

The compounds having an intramolecular charge transfer properties are usually functionalized by electron-donating (D) and electron-accepting (A) groups through an azo π-conjugated bridge which makes it possible to reduce the gap between HOMO and LUMO of the molecule for broadening the range of absorption and to study the relationship between the variation of donor/acceptor chromophores and their corresponding photophysical and electrochemical properties [7]. The electron-rich N,N-diethylaniline unit is one of the promising donor moiety of donor–acceptor type of functional molecules because of its good electron-donating properties. The presence of acetamido groups at ortho position

relative to the azo bridge is attributed to the hydrogen bonding with azo groups [8]. Also, acetamido and ester moieties are helpful to increases their light fastness, color strength and bright hue as well as photostability properties [9,10].

In this paper, we report synthesis of disperse azo dyes by using traditional azo coupling between N,N-diethyl substituted aniline as a coupler and diazonium salt dimethyl 2-amino-5-nitroterephthalate [11]. Density functional theory computations [B3LYP/6-31G(d)] were used to study the geometrical and electronic properties of the synthesized molecules. The solvent effect on absorbance characteristics of the synthesized azo dispersed dyes were studied in solvents of different polarities.

2. Experimental section

2.1. Materials and equipments

Dimethyl 2-aminoterephthalate, N,N-diethylaniline, N-(3-(diethylamino)phenyl) acetamide, N-(3-(diethylamino)-4-methoxyphenyl) acetamide, sodium hydroxide, metamol (dispersing agent) and conc. H_2SO_4 were purchased from s.d. fine chemicals Ltd, Mumbai, India. Solid reagents were characterized by melting point and used without further purification. Liquid reagents distilled at their boiling points and used thereafter. Solvents were used after distillation at their boiling point and drying according to standard processes.

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All the reactions were monitored on precoated silica gel aluminum based plates kisel gel 60 F$_{254}$ Merck, India. Purification of all the compounds was achieved by recrystallization. Melting points were recorded on instrument from Sunder Industrial Product Mumbai by using open capillary and are uncorrected. The absorption spectra of the compounds were recorded on a Spectronic Genesys 2 UV—visible spectrophotometer. The FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ^{1}H NMR spectra were recorded on a Varian Cary Eclipse Australia, USA instrument using TMS as an internal standard. Mass spectra were recorded on Finnigan Mass spectrometer. The chemical shift values are expressed in δ ppm using CDCl$_3$ as a solvent and TMS as an internal standard. DFT calculations were performed on a HP workstation XW 8600 with Xeon processor, 4 GB RAM and Windows Vista as operating system. The software package used was Gaussian 09W. The ground state geometry was optimized at B3LYP level of theory and 6-31G (d) as basis set.

2.2. Computational methods

Gaussian 09 program package was used to optimize geometry and to study the synthesized azo dyes in their azo and hydrazone tautomeric forms [12]. Ground state (S0) geometry of the dyes in gas and solvent was optimized in their C1 symmetry using DFT [13]. The Becke's three parameter exchange functional (B3) [14] combining with nonlocal correlation functional by Lee, Yang and Parr (LYP) [15] and basis set 6-31G (d) was used for all atom. Same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. Time Dependent Density Functional Theory (TD-DFT) computations were used to obtained the vertical excitation energies and oscillator strengths at the optimized ground state equilibrium geometries at the same hybrid functional and basis set [16]. All the computations in solvents of different polarities were carried out using the Self-Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM) [17].

2.3. Synthesis and characterization

The synthetic scheme for the preparation of dyes **7a**—**7c** is shown in Scheme 1. Dimethyl 2-amino-5-nitroterephthalate **(5)** was prepared by the reported procedure [18] from dimethyl 2-aminoterephthalate **(1)**.

2.3.1. Preparation of azo dyes (7a—7c)

2.3.1.1. Preparation of diazotization salt **(6)**. A solution of dimethyl 2-amino-5-nitroterephthalate **5** (2.5 g, 0.01 mol) in concentrated sulfuric acid (10 ml) was slowly added to 1.56 M nitrosylsulfuric acid at 0—5 °C within 1 h. Diazotization reaction was monitored using starch iodide paper. 0.02 g of urea was added to consume excess of nitrous acid. The resulting diazonium solution **6** was further used immediately for coupling.

2.3.1.2. General procedure for coupling. The coupler **a**—**c** (0.01 mol) were dissolved in 150 ml ethanol at 0—5 °C. Diazonium solution was added dropwise to coupler at 0—5 °C and 5—6 pH adjusted by using 10% sodium hydroxide cold solution. The reaction mixture was further stirred overnight and monitor by using H-acid and starch iodide paper. Precipitated product was filtered and washed with water, crystallized from ethanol to give dyes **7a**—**7c** respectively.
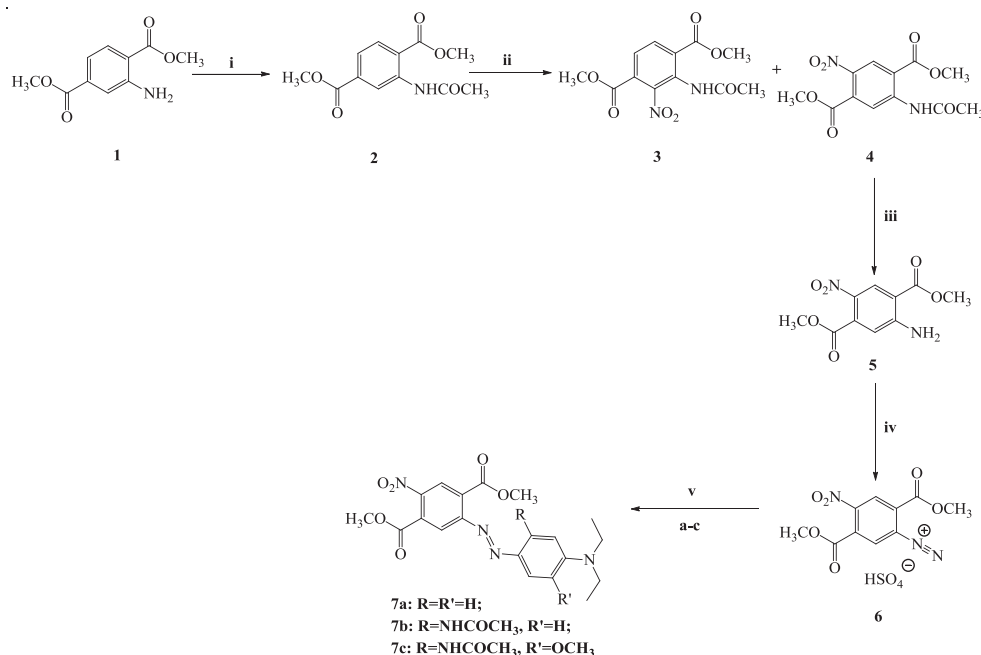
*(E)-Dimethyl 2-((4-(diethylamino)phenyl)diazenyl)-5-nitroterephthalate **(7a)***

Yield: 72%, **Melting Point**: 40—42 °C.

FAB-MS, *m/z*: 415.67 [M + H]$^+$,

HRMS (FAB+) *m/z*: calcd for [M + H]$^+$, 415.1618; found, 415.1617.

^{1}**H NMR (CDCl$_3$, 600 MHz):** 8.26 (s, 1H, Ar—H), 7.99 (s, 1H, Ar—H), 7.86 (d, 2H, Ar—H, *J* = 9 Hz), 6.74 (d 2H, Ar—H, *J* = 9 Hz),

Reaction condition: (i) Acetic anhydride, Toluene, 80 ^{0}C. **(ii)** Concentrated H$_2$SO$_4$, Fuming HNO$_3$, 0-5 ^{0}C.
(iii) Concentrated H$_2$SO$_4$, Methanol, 80 ^{0}C, 2hr. **(iv)** Nitrosylsulfuric acid, 0-5 ^{0}C.
(v) Ethanol, pH 5-6, 0-5 ^{0}C to room temperature.

Scheme 1. Synthesis of azo disperse dyes **7a**, **7b** and **7c**.