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Photophysical and theoretical studies on newly synthesized *N*,*N*-diphenylamine based azo dye

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The azo-hydrazone tautomerism, solvatochromism and halochromism in diphenylamine based azo dye ((*E*)-1-(4-((4-(phenylamino)phenyl)diazenyl)phenyl)ethanone, **DPA**) were examined. The absorption wavelengths of the dye in different solvents were in the range 429–544 nm. The compound exhibits positive solvatochromism as the absorption band is red shifted with increasing solvent polarity. In addition, the absorption properties of the dye change drastically upon acidification, as the protonation of β-nitrogen atom of the azo group increases the donor-acceptor interplay of the π system. The experimental results are fully supported by DFT and TD-DFT calculations. Moreover, nonlinear optical properties (NLO) were also obtained by the theoretically predicted values of dipole moment (μ), polarizability (α) and first hyperpolarizability (β).

1. Introduction

Azo dyes are the largest group of class of organic dyes. They have high dyeing and good fastness properties and can be easily, and inexpensively obtained using a wide variety of diazo and coupling components [1]. They constitute more than 50% of the global textile dyes production of all dyes and thus are used widely because of their strong tinctorial strength compared to anthraquinone dyes, ease to make, and a low cost of manufacture [2]. Furthermore, they are also used in the fields of NLO, optical data storage, advanced applications in organic synthesis, biological-medicinal studies and in analytical chemistry as acid-base, redox and metallochromic indicator and sensor [3–11]. Azo dyes have been also widely used for the development and testing of colour theories and constitution, tautomerism, indicator action and acid–base equilibrium [12–17] and, as such, the study of azo dyes has been of great value in the development of theoretical organic chemistry. The majority of commercially important azo colorants contain a single azo bridge. Therefore, the synthesis and investigation of spectroscopic, electrochemical, tautomeric, optical properties of many commercially important monoazo dyes especially those bearing *N*,*N*-dialkyl/arylamine as coupling component have been studied in the past decades [18–33] (Scheme 1).

In this study, we describe the azo dye (**DPA**) containing acetyl group in the para-position of diazo component and as coupling component of *N*,*N*-diphenylamine core in order to make an impact on bathochromism and solvatochromism of the azo dye through extending conjugation and increasing electron accepting/donating strength. It was synthesized and characterized by IR, UV–vis, ^{1}H NMR, ^{13}C NMR and HRMS techniques. We investigated the influence of solvents of different polarities and acid on the UV–vis absorption spectra of **DPA.** The density functional theory (DFT) and time-dependent DFT (TD-DFT) methods were employed to obtain the geometrical and electronic properties of **DPA**. In addition, DFT calculations were performed to obtain NLO properties of **DPA**.

2. Experimental

2.1. Materials and instrumentation

The chemical used in the synthesis of the compound was

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C.I. Disperse Red 1 **C.I. Disperse Red 13**

C.I. Disperse Orange 1 **4-(Phenylazo)diphenylamine (PDA)**

Scheme 1. Some representative azo dyes bearing *N*,*N*-dialkyl/arylamine as coupling component.

procured from the Aldrich Chemical Company and used without further purification. The solvents were used of spectroscopic grade. FT-IR (ATR) spectra were recorded on Nicholet IS 50 FT-IR spectrophotometer (ν, are in cm^{-1}). NMR spectra were recorded on a Bruker-SpectrospinAvance DPX 300 Ultra-Shield in DMSO-d_6 and $CDCl_3$. Chemical shifts are expressed in δ units (ppm). Ultraviolet–visible (UV–vis) absorption spectra were recorded on Shimadzu Corporation, Kyoto Japan UV-1800 240V spectrophotometer at the wavelength of maximum absorption (λ_{max}, in nm) in the solvents specified. Mass spectra were recorded on Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments; in *m*/*z* (rel. %) (Gazi UniversityLaboratories, Department Pharmacological Sciences). Chemical shifts are expressed in δ units (ppm) with tetramethylsilane (TMS) as the internal reference. Coupling constant (*J*) is given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; triplet, t; multiplet, m.

2.2. Preparation of (E)-1-(4-((4-(phenylamino)phenyl)diazenyl)phenyl)ethanone

2.0 mmol (0.27 g) of 4-aminoacetophenone was dissolved in hydrochloric acid (1.5 mL conc. HCl in 4 mL water). The solution was then cooled to 0–5 °C with stirring. Sodium nitrite (0.15 g, 2.0 mmol) in water (3 mL) was gradually added to this solution over 15 min period at temprature range of 0–5 °C while stirring. The mixture was stirred for an additional 1 h while maintaining it at temprature range of 0–5 °C. Excess nitrous acid was destroyed by the addition of urea. Diphenylamine (2.0 mmol, 0.34 g) was dissolved in acetic acid/propionic acid (4 mL, ratio 3:1) and cooled to temprature range of 0–5 °C in a salt/ice bath. The cold diazonium salt solution was added to this cooled solution over for 1 h with vigorous stirring in a drop-wise manner, while maintaining the pH between 4 and 6 by the addition of saturated potassium hydroxide solution. The mixture was further stirred for 1 h at temprature range of 0–5 °C and the resulting solid was filtered, washed with cold water, dried, and crystallized from ethanol as orange crystal (yield: 0.33 g, 52%; m.p: 184–186 °C); FT-IR (ATR, $\upsilon_{max.}$, cm^{-1}): 3346 (N–H), 1664 (C=O), 1586 (aromatic C=C); ^1H NMR (DMSO-d_6, 300 MHz): $^{\delta}H$ 9.0 (s, 1H), 8.1 (d, *J* = 8.54 Hz, 2H), 7.90-7.85 (m, 4H), 7.40 (t, 2H), 7.35 (d, *J* = 7.50 Hz, 2H), 7.25 (d, *J* = 8.95 Hz, 2H), 7.05 (t, 1H), 2.60 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz): δ_C 197.5, 155.6, 147.6, 147.4, 146.4, 140.8, 137.5, 129.5, 129.3, 125.5, 123.2, 122.4, 120.4, 117.8, 111.4, 26.8 ppm; HRMS (ESI, CH_3CN) ($C_{20}H_{18}N_3O$) found: 316.1436, calcd.: 316.1450.

2.3. Computational study

The structures of the azo and hydrazone, and the cationic form of **DPA** were optimized using Gaussian 09 program [34]. The density functional theory (DFT) was employed in all calculations with the B3LYP functional, in which Becke's nonlocal exchange [35,36] and the Lee-Yang-Parr correlation functionals [37]. The vibrational frequencies were calculated at the same theoretical level to confirm that all optimized ground configurations had no imaginary frequencies and were minima on potential energy surfaces. The structure is also optimized in different solvent using the polarized continuum model (PCM) [38,39]. The basis set 631G(d,p) was used in all calculations. Absorption spectra were computed as vertical electronic excitations from the ground-state minima by using the time-dependent density functional theory (TD-DFT) [40]. The absorption maxima and oscillator strengths were obtained for the lowest 10 singlet–singlet transitions. In addition, the linear polarizability and first hyperpolarizability properties of **DPA** were obtained from molecular polarizabilities based on theoretical calculations.

3. Results and discussion

3.1. Synthesis

DPA was prepared by coupling the reaction of *N*,*N*-diphenylaniline with 4-aminoacetophenone in dilute hydrochloric acid (Scheme 2). The structures of the prepared dye have been confirmed by FT-IR, UV–vis, ^1H NMR, ^{13}C NMR and HRMS techniques. Spectroscopic data of the prepared dye are given in Table 1. The dye may exist in two possible tautomeric forms (azo-hydrazone) in neutral condition as outlined in Scheme 3. In addition, the protonation of tautomers with trifluoroacetic acid (TFA) leads to azonium-amonium tautomeric forms (Scheme 4).

The IR spectrum of the prepared dye showed two characteristic bands at 3346 and 1664 cm^{-1}, corresponding to amine (N–H) and carbonyl (C=O), respectively. In the ^1H NMR spectra of the studied dye, the NH peak was observed at lower field in DMSO-d_6 than in $CDCl_3$. It was observed at 9.0 ppm in DMSO-d_6 and at 6.0 ppm in $CDCl_3$. NH proton signal shifts lower field in DMSO-d_6 compared with $CDCl_3$, probably because of the intermolecular hydrogen bond between the NH and DMSO (Fig. S1 and S2). In addition, it can be clearly seen that the ^{13}C NMR (APT) spectra of **DPA** are same completely in $CDCl_3$ and DMSO-d_6 (Fig. S3 and S4). There are no evidence of hydrazone tautomeric form of dye in NMR spectra in $CDCl_3$ and DMSO-d_6, thus it may exist in azo tautomeric form in these solvents.