SYNTHESIS AND CHARACTERIZATION OF SOME NEW AZO COMPOUNDS BASED ON 2, 4-DIHYDROXY BENZOIC ACID

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Abstract

A series of four new azo dyes have been synthesized by coupling 2,4-dihydroxybenzoic acid with m-nitroaniline (I), p-aminobenzoic acid (II), p-aminophenol (III) and p-toluidine(IV). The chemical structure of the newly prepared azo compounds was characterized by elemental analysis, IR and 1H-NMR spectra. The electronic absorption spectra had been investigated in ethanol and organic solvents of varying polarities. The important IR bands, 1H-NMR signals and absorption bands in the UV-visible region were assigned and discussed in relation to molecular structure. The absorption spectra of the azo compounds were studied in buffer solution of varying pH values containing 30% (v/v) ethanol from which the corresponding pK_H values were determined.

1. Introduction

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time. In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts [1, 2]. Azo compounds are considered as class of organic colorants which consist of at least a conjugated chromophore azo (-N=N-) group in association with one or more aromatic or heterocyclic system [3, 4]. They are capable of providing high intensity color and have reasonably good technical properties, including light and weather fastness and resistance to solvents and water [5]. The biological importance of azo compounds is well known due to their use as inflammatory [6, 7], and anticancer [8, 9], antifungal. Azo compounds are important structures in the medicinal and pharmaceutical fields [10, 11] also, they have received much attention due to their versatile use in many practical applications such as coloring fiber [12, 13], printing systems [14], optical storage technology [15], photoelectronic applications, and in various analytical techniques [16 - 18]. The azo compounds also find their wide applications as a polymer additive [19]. Furthermore, azo dyes have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium [20]. It have also attracted attention due to their interesting electronic features in connection with their application for molecular memory storage,

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nonlinear optical elements and organic photoconductors [21, 22].

The present paper reports the synthesis and characterization of four new azo compounds using elemental analysis, IR, 1H-NMR, and electronic spectral techniques in organic solvents and in buffer solution of different pH values. The acid ionization constant (pKₐ) were also determined.

2. Experimental

All chemicals used in this study are of highly pure products from (Fluka, Aldrich and Adwic products) and were used without further purification. All solvents are used and obtained with highly purity from Merck Company.

The azo compounds were prepared by coupling of 2,4-dihydroxybenzoic acid (in sodium hydroxide) with the diazonium salts of the corresponding aniline derivatives (m-nitroaniline, p-aminobenzoic acid ,p-aminophenol and p-toluidine).

0.01 mole of the aromatic amines were converted to the hydrochloric form by adding the least amount of 1:1 HCl then diluting with water and cooling at -2.0°C. A cooled solution of NaNO₂ (0.01 mole) was added gradually with continuous stirring to the amine salt. The resulting diazonium salt solution was allowed to stand in ice bath for 15 min with stirring at -2.0 °C and added gradually to a solution of 0.01 mole of 2,4-dihydroxybenzoic acid dissolved in 10% NaOH which cooled at -2.0°C. The resulting solution was allowed to stand for 15 min with constant stirring until the azo dye completely formed.

The azo compounds obtained is filtered off, dried and recrystallized from ethanol. The purity of the resulting azo compounds was checked by the melting point constancy. The chemical structure of the azo compounds is detected by elemental analysis (C, H, N), IR and 1H-NMR spectra. They have the following structural formula:

![Structural formula of azo compounds]

X= m̅NO₂ (I), p COOH (II), p OH (III) and p (CH₃) (IV)

Solutions of the dyes (10⁻³ M) were prepared in the appropriate volume of pure solvent. Solutions for spectral measurements were obtained by appropriate dilution of the stock ones.

Electronic spectra were measured using Jasco V-530 (UV-VIS) spectro-photometer (Japan). The IR spectra were recorded as KBr disk technique on a Beckmann IR 4220 spectrophotometer and the ¹H-NMR spectra were recorded on a Varian EM 390-90 MHz NMR spectrometer using tetramethylsilane (TMS) as internal standard and DMSO-d₆ as a solvent.
3. Results and Discussion

The purity of the compounds (I-IV) was firstly confirmed by m.p. constancy. Their elemental analysis (c.f. Table 1) showed satisfactory agreement with the expected tentative formula.

Table (1): Elemental analysis of the azo compound under investigation.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>color</th>
<th>m.p. (^{\circ}C)</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>Tentative formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>L1</td>
<td>Red</td>
<td>173</td>
<td>51.49</td>
<td>51.17</td>
<td>2.99</td>
<td>2.65</td>
</tr>
<tr>
<td>L2</td>
<td>Brown</td>
<td>192</td>
<td>55.63</td>
<td>55.48</td>
<td>3.33</td>
<td>3.19</td>
</tr>
<tr>
<td>L3</td>
<td>Orange red</td>
<td>187</td>
<td>56.94</td>
<td>56.62</td>
<td>3.68</td>
<td>3.24</td>
</tr>
<tr>
<td>L4</td>
<td>Black brown</td>
<td>185</td>
<td>61.76</td>
<td>61.37</td>
<td>4.44</td>
<td>4.25</td>
</tr>
</tbody>
</table>

3.1. IR Spectra:

The assignment of the IR absorption bands was carried out by a method similar to that suggested by Looker [23] in which the spectral region is divided to three main regions mainly; 4000 – 2600, 1700 – 1200, and 1000– 625 cm\(^{-1}\).

In the first region, the broad band appearing at 3377 – 3419 cm\(^{-1}\) in all the compounds corresponds to the stretching vibrations of the OH and CH groups. Two bands at 3076 – 2858 cm\(^{-1}\) is attributed to the asym and sym stretching vibrations of the CH groups. This was recognized by Coblenz [24] and Bonino [25] who pointed out that the characteristic C-H bands of aromatic and aliphatic compounds occur at different recognizable positions in this region. Compound (IV) shows a band at 2549 cm\(^{-1}\) due to the stretching vibration of the CH\(_3\) group. The weak band at 2864 cm\(^{-1}\) found in compound (II) and (III) is due to the stretching vibration of the NH group resulting from the quinone ↔ hydrazine tautomerism taking place as follow:

![Diagram of IR Spectra](image-url)
In the second region, the bands at 1625 – 1624 and 1526 – 1513 cm\(^{-1}\) can be attribute to the stretching vibrations of the C=O and the C=C ring absorption bands, respectively. The stretching vibration of N=N bond gives rise to a band at 1443 – 1428 cm\(^{-1}\) while the bending vibration band of the OH group appears at 1230 – 1216 cm\(^{-1}\).

In the last region, most of the strong bands appearing in the range 1000 – 625 cm\(^{-1}\) are due to the out – of – plane deformation vibration of the hydrogen atoms present in the ring. The band position can be discussed in terms of the number of adjacent hydrogen atoms. The weak to medium bands at 848 – 835 cm\(^{-1}\) are assigned to the out – of – plane C-H deformation of two adjacent hydrogen atoms. In the spectrum of compound (I), the strong band at 729 cm\(^{-1}\) is due to the deformation vibration of three adjacent hydrogen atoms.

\(^1\)H-NMR Spectra

The \(^1\)H-NMR spectrum of compound (IV) shows a singlet signal at \(\delta = 2.35\) ppm (s; 3H) due to the three protons of the methyl group in p- position to the N=N group. The signal of the OH group in o-position to the carboxylic group in the 2,4-dihydroxybenzoic acid moiety shows a doublet signals at \(\delta = 6.19 – 6.28\) ppm, while that of the second hydroxyl group in p-position to the COOH group shows singlet signals at \(\delta = 6.20 – 6.28\) ppm. For compound (III), the OH group in p-position to the azo linkage shows singlet signal at \(\delta = 6.33\) ppm. All these signals are removed by deuteration. The \(^1\)H-NMR spectra of all compounds show doublet signal at \(\delta = 10.35-10.40\) ppm due to the proton of the COOH group. Multiple signals of the aromatic protons appear in the range 6.65 – 7.80 ppm.

3.2. Electronic Absorption Spectra in Ethanol

The absorption spectra of the azo compounds under investigation were recorded in ethanol within the range 200 – 600 nm. The spectra display mainly four absorption bands (c.f. Fig. 1).

![Fig (1): Electronic absorption spectra of compounds (I-IV) in ethanol](image-url)
The first two bands found in the range 203 – 245 nm are assigned to the medium and low energy π – π* transitions within the aromatic moieties representing the (1Lₐ→1A) and (1Lₖ→1A) states respectively. This is confirmed by the high values of molar extinction coefficient (ε; dm³ mol⁻¹ cm⁻¹) amounting to 3.55×10⁴ – 4.51×10⁵. The third band appears at λ = 295 nm is due to the n-π* transition of the C=O and/or the N=N group [26]. The fourth band located at longer wavelength side (λ > 400 nm), being sensitive to both solvent polarity and nature of substituent, can be assigned to the π – π* transition within the azo group involving charge transfer (CT) interaction through the whole molecule represented as:

It is worthy to mention that, the relatively shorter wavelength at which the CT band takes place is expected due to the formation of an intramolecular hydrogen bond between the OH group in o-position to the COOH group forming a stable five - membered ring.

3.3. Solvent Effect:

The absorption spectra of the azo compounds under study were scanned in different solvents of varying polarities; ethanol, methanol, dimethylformamide (DMF), diethylether, acetone and benzene (representative example is shown in (Fig. 2).

Fig (2): Absorption spectra of compound (I) in different organic solvent
Inspection of Fig (2) shows that, bands due to the local π-π* transition in the UV region display an irregular solvent shift, yet the general trend is a red shift with increased solvent polarities. This behavior is characteristic of the π-π* transition of the substituted benzenes where the solvent substituent interaction would be additive or counteracts the solvent shift of the aromatic nucleus [27]. On the other hand, the longer wavelength band corresponding to the intramolecular CT interaction displays some shifts in all solvents studied.

To assess the influence of the solvents on the CT band, the so-called macroscopic and microscopic solvent polarity parameters were applied. The plots of Δν (cm⁻¹) vs (D-1)/(D+1) [28], and λ_max (nm) vs f(D), φ(D) [29], π, α, β [30], E_T and Z [31,32] values gave nonlinear relations. This indicates that none of such parameters solely is the predominating factor affecting the position of the CT band, but contribution of specific solute – solvent interaction (salvation or more effectively hydrogen bonding between solute and solvent molecules) also takes place. So, the shift in the CT band position is actually the result of changed solvent polarity and the shift due to intermolecular hydrogen bond.

3.4. Spectra in Buffer Solutions

The acid ionization constants (pK_H) of the azo compounds under investigation are determined spectrophotometrically in universal buffer solutions covering the pH range 2.20 – 12.03. The absorption spectra of the compounds in buffer solutions of varying pH values are recorded within the wavelength range 340 – 600 nm. The acid ionization constants (pK_H) were calculated using Half – height [33], and Modified isosbestic [34] methods. Representative example of the absorption spectra is shown in Fig (3) and the pK_H values are cited in Table (2).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Ionization constant</th>
<th>Average (λ_max: nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>pK_H</td>
<td>9.35 (375)</td>
</tr>
<tr>
<td>II</td>
<td>pK_H</td>
<td>8.60 (385)</td>
</tr>
<tr>
<td>III</td>
<td>pK_H</td>
<td>5.56 (376)</td>
</tr>
<tr>
<td>IV</td>
<td>PkH</td>
<td>7.78 (370)</td>
</tr>
</tbody>
</table>

The absorption spectra of 1x10⁻⁴ M solutions of compounds (I-IV) exhibit bands located at ≈ 340 nm due to charge transfer interaction within the whole molecule. The intensities of these bands decrease and suffer red shift leading to a band at 480 nm with increasing pH with clear isosbestic point at ≈ 425 nm. This indicates an equilibrium state between two forms of the compound due to the deprotonation of the COOH and OH groups.
Fig (3): Absorption spectra of compound (III) in buffer solution

The variation of absorbance of solution with pH are nearly S – shaped as shown in Fig.(4-a) while applying the modified limiting absorbance method gives straight line intercept with the zero point of log(A_{\text{Amin}})/(A_{\text{max}}-A) axis at the corresponding pK_H value as shown in Fig.(4-b).
Fig (4): Variation of absorbance of solution with pH
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References


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