SYNTHESIS AND ABSORPTION CHARACTERISTICS OF SOME DISAZO DYES DERIVED FROM 4-AMINO-3-NITROTOLUENE AND 4-AMINOBENZOIC ACID

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ABSTRACT

The synthesis of a series of 4-amino-3-nitrotoluene dye derivatives has been carried out. Diazotization and coupling with 4-aminobenzoic acid gave an intermediate diazo component. Coupling reactions of the diazotized diazo component with 2-methylphenol, 4-hydroxybenzoic acid, chromotropic acid, 4-aminophenol and 4-chloroaniline gave various disazo dyes. The results of the half-band widths showed that although they are disazo dyes they can compete favourably with most monoazo and anthraquinone dyes in terms of hue brightness. The solvatochromism of the dyes was evaluated with respect to spectroscopic properties in various solvents. The dyes were characterized by elemental analysis and spectral methods.

Keywords: Disazo dyes, absorption Characteristics, Tautomerism, Solvatochromic effect.

INTRODUCTION

The use of carbocyclic compounds to prepare disazo dyes for colouring textile and non-textile materials is important due to their increased wash fastness and substantivity (Shuttleworth and Weaver, 1990; James et al., 1982). Many non-ionic organic azo pigments such as C.I. (Colour Index) Pigment Yellow 1, Pigment Orange 6 and Pigment red 3 have been prepared from the carbocyclic compound; 4-amino-3-nitrotoluene (Allen, 1971). They are used largely in paints and printing inks. Our research has recently reported some aspects of the preparation and application of certain novel azo disperse dyes involving the use of this intermediate (Otutu, 2008). Dyeing with such disazo disperse dyes of this type gave very good light fastness property on poly (ethylene) terephthalate, using the thermosol process. Also, the disazo dyes containing the 2-aminophenyl group showed excellent levels of fastness (wash and sublimation) on poly (ethylene) terephthalate and nylon fibres. Here we report the synthesis of a new series of disazo dyes from 4-amino-3-nitrotoluene and 4-aminobenzoic acid. We also describe the solvatochromic behaviour of these dyes in various solvents.

MATERIALS AND METHODS

Materials

4-Amino-3-nitrotoluene, 4-aminobenzoic acid, 2-methylphenol, 4-hydroxybenzoic acid, chromotropic acid, 4-aminophenol and 4-chloroaniline were obtained from BDH Chemical Company and Aldrich Chemical Company and used without further purification.

Methods

Synthesis of diazo component 3 (Scheme 1)

A finely ground powder of the 0.05mole (8.0 g) 4-amino-3-nitrotoluene was mixed with 50 ml of water and cooled to 0 - 5°C and diazotized with 5.0 g, 0.0725 mole of NaN02 at 0°C in concentrated sulphuric acid (10 ml). The 4-aminobenzoic acid (0.05 mole 7.5 g) which was dissolved in 60 ml acetic acid was coupled with the diazonium salt solution at pH values 4 – 5. The mixture was stirred for a further 2 hours and left to stand overnight at 40°C in an incubator. The crude product was collected by filtration, washed with water several times and dried. The purity of the dyes was determined by Thin Layer Chromatgraphy (TLC). The yield of the reac-
The purification was 75% after the recrystallization of the crude product from carbontetrachloride.

**Scheme 1**

\[
\begin{align*}
\text{H}_2\text{C} - \text{NH}_2 & \xrightarrow{\text{H}_2\text{SO}_4/\text{NaNO}_2, 0 - 5^\circ\text{C}} \text{H}_2\text{C} - \text{N} \equiv \text{N} \\
\text{NO}_2 & \xrightarrow{\text{2 CO}_2\text{H}} \text{H}_2\text{C} - \text{N} \equiv \text{N} - \text{NH}_2 \\
\text{NO}_2 & \xrightarrow{\text{3 H}_2\text{SO}_4/\text{NaNO}_2, 0 - 5^\circ\text{C}} \text{R}
\end{align*}
\]

**Scheme 2**

**Synthesis of dye 5a**

2-Nitro-4-methylphenylazo-4'-aminobenzene was suspended in 45 ml of water and diazotized with (0.04 mole, 3.0 g) of sodium nitrite (in 10 ml water) at 0 - 5°C and diazotized with (0.0536 mole 3.7 g) of NaNO₂ at 0°C in concentrated sulphuric acid (6 ml). The 0.04 mole, (0.5 g) 4-chloroaniline which was dissolved in (20 ml) acetic acid was coupled with the diazonium salt above at pH values 4 – 5. After stirring for 2 hours, the crude product was collected by filtration, washed with water and dried. Recrystallization from hot ethanol-methanol mixture gave compound 5a in 51% yield. The purity of the dye was assessed by TLC (ether/aceton 5:1 by volume). This procedure was also used to prepare dye 5b, 5c and 5d.

**Synthesis of dye 5e**

A finely ground powder of 2-nitro-4-methylphenylazo-4'-aminobenzene (0.006 mole 1.50 g) was mixed with 50 ml of water, cooled to 0 - 5°C and diazotized with (0.0536 mole 3.7 g) of NaNO₂ at 0°C in concentrated sulphuric acid (6 ml). The 0.04 mole, (0.5 g) 4-chloroaniline which was dissolved in (20 ml) acetic acid was coupled with the diazonium salt above at pH values 4 – 5. After stirring for 2 hours, the crude product was collected by filtration, washed with water and dried. Recrystallization from hot ethanol-methanol mixture gave compound 5e in 50% yield. Dye purity was determined by TLC (ether/aceton 5:1 by volume).

**Chemical and Instrumental Analysis**

Melting points were determined without correction using the Thumbnail melting point apparatus. The ¹H NMR spectra were taken with a mercury – 200BB (200 MHz) spectrometers using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are expressed as δ units (ppm). Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet Averser 330 series spectrophotometer. The UV-visible spectra were recorded in 1cm quartz cells on a Genesy 1S VL 200 series spectrophotometer. Elemental analysis was determined using Perkin Elmer 2400 series for CHN. Dye purity was assessed by Thin Layer Chromatography (TLC) using Whatman 250m silica gel 60AMK 6F plates as the stationary phase and ether/aceton 5:1 by volume mixture as developing solvent. The characterization data are shown in Tables 1 and 2.
Table 1: FTIR and 'H NMR data of dyes 5a-e

<table>
<thead>
<tr>
<th>FTIR (ν/cm-1)</th>
<th>'H NMR (ppm)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a 1658 (N-H)</td>
<td>6.09 (s, 1H, phenyl proton)</td>
<td>CDCl3</td>
</tr>
<tr>
<td>2730 (Aromatic C=C)</td>
<td>6.02 (d, 1H, phenyl proton)</td>
<td></td>
</tr>
<tr>
<td>1826 (Aromatic C-H)</td>
<td>6.09 (s, 1H, phenyl proton)</td>
<td></td>
</tr>
<tr>
<td>1504 (Aromatic C=O)</td>
<td>6.09 (s, 1H, phenyl proton)</td>
<td></td>
</tr>
<tr>
<td>1275 (C–O)</td>
<td>6.09 (s, 1H, phenyl proton)</td>
<td></td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Azo-hydrazone tautomers**

The existence of hydroxyazo-ketohydrazone tautomers not only have different colours, they also have different tautomeric strengths (and hence economics) and different properties (Ortega-Luoni et al., 2007).

In addition, it has been found that, compared with the hydroxyazo tautomer, the corresponding ketohydrazone tautomer is usually more bathochromic and of higher tautomeric strength. The tautomeric equilibrium position of hydroxyazo-ketohydrazone systems varies according to the chromophore, the nature and position of substituents, the solvent or the substrate, the temperature and various other factors (Zollinger, 2003; Samieh et al., 2008; Zeynel, 2009). In general, however, either the hydroxyazo tautomer or the corresponding ketohydrazone tautomer or the corresponding ketohydrazone formed is dominant for a particular structure. Azo dyes 5a – e can exist as a mixture of several tautomeric forms as shown in scheme 3.

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**Table 2: Yields, melting points and Elemental analysis of dyes 5a-e**

<table>
<thead>
<tr>
<th>Dye</th>
<th>R</th>
<th>Yield (%)</th>
<th>M.P/(°C)</th>
<th>Elemental analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>-</td>
<td>51</td>
<td>228 – 230</td>
<td>63.99 4.56 18.66</td>
</tr>
<tr>
<td>5b</td>
<td>-</td>
<td>60</td>
<td>168 – 170</td>
<td>63.15 4.18 19.38</td>
</tr>
<tr>
<td>5c</td>
<td>-</td>
<td>54</td>
<td>183 – 185</td>
<td>43.71 2.34 11.06</td>
</tr>
<tr>
<td>5d</td>
<td>-</td>
<td>56</td>
<td>182 – 184</td>
<td>60.61 4.28 22.33</td>
</tr>
<tr>
<td>5e</td>
<td>-</td>
<td>50</td>
<td>193 – 195</td>
<td>57.66 3.63 21.29</td>
</tr>
</tbody>
</table>

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Renfrew, 1996: The hydroxyazo-ketohydrazone tautomers not only have different colours, they also have different tautomeric strengths (and hence economics) and different properties (Ortega-Luoni et al., 2007).

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**Diagram**

5a: Hydroxyazo tautomer
5b: Ketohydrazone
5c: Hydroxyazo tautomer
5d: Ketohydrazone
5e: Ketohydrazone
The infrared spectra of dyes 5a – d showed a broad hydroxyl band at 3467 – 3522 cm\(^{-1}\) and a C-O band at 1272 – 1275 cm\(^{-1}\). This suggests that these compounds are predominantly in the hydroxyazo form, as opposed to the hydrazone-keto form in the solid state.

On the other hand, the infrared spectra of dyes 5c and 5d showed intense carboxyl bands in DMF were determined and the results showed predominantly in a single tautomeric form in ethanol (ETOH) and chloroform (CHCl\(_3\)). As dyes 5a – d gave maximum absorption peak with a shoulder in DMF, it suggests that these dyes were present in more than one tautomeric form.

It was observed that although, in chloroform and N,N-dimethylformamide the absorption spectra did not change significantly, \(\lambda_{\text{max}}\) of dyes 5a – e shifted bathochromically in ethanol. On the other hand, it was observed generally, that \(\lambda_{\text{max}}\) values of the dyes shifted bathochromically with respect to the \(\lambda_{\text{max}}\) in chloroform and N, N-di methylformamide.

### Table 3: Influence of solvent on UV-visible absorption spectra of dyes 5a–e

<table>
<thead>
<tr>
<th>Dye</th>
<th>ETOH</th>
<th>CHCl(_3)</th>
<th>DMF</th>
<th>(\Delta\nu\text{(\frac{1}{2})}) ETOH</th>
<th>(\Delta\nu\text{(\frac{1}{2})}) CHCl(_3)</th>
<th>(\Delta\nu\text{(\frac{1}{2})}) DMF</th>
<th>(\epsilon_{\text{max}}) ETOH</th>
<th>(\epsilon_{\text{max}}) CHCl(_3)</th>
<th>(\epsilon_{\text{max}}) DMF</th>
<th>(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>433</td>
<td>4425</td>
<td>440,580(x)</td>
<td>8.9000</td>
<td>21900</td>
<td>8.231</td>
<td>9.282</td>
<td>32.543</td>
<td>8.989</td>
<td>11.093</td>
</tr>
<tr>
<td>5b</td>
<td>427</td>
<td>4425</td>
<td>438,580(x)</td>
<td>8.1000</td>
<td>31600</td>
<td>9.282</td>
<td>32.543</td>
<td>8.989</td>
<td>11.093</td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>438</td>
<td>4435</td>
<td>448,580(x)</td>
<td>8.1000</td>
<td>93000</td>
<td>32.543</td>
<td>8.989</td>
<td>11.093</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5d</td>
<td>436</td>
<td>4455</td>
<td>446,580(x)</td>
<td>8.1000</td>
<td>30600</td>
<td>8.989</td>
<td>11.093</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5e</td>
<td>430</td>
<td>4465</td>
<td>4405</td>
<td>7.4000</td>
<td>34700</td>
<td>8.989</td>
<td>11.093</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = Shoulder

Oscillator strength \((f) = 4.32 \times 10^9 \times \Delta\nu\text{\(\frac{1}{2}\)} \times \epsilon_{\text{max}}\)

### Half-band widths

The half-band widths of the absorption bands in DMF were determined and the results are shown in Table 3. The value of half-band widths, \(\Delta\nu_{\frac{1}{2}}\) is a very important criterion for the determination of the hue brightness of dyes; thus, dyes with low values of \(\Delta\nu_{\frac{1}{2}}\) exhibit bright hues while those with high values of \(\Delta\nu_{\frac{1}{2}}\) show dull hues. From the results of the \(\Delta\nu_{\frac{1}{2}}\) values of dyes 5b, 5d and 5e respectively showed narrower half-band widths than dyes 5a and 5c, which means that the former dyes in solvent are brighter than the latter analogues in solvent. However, the correlation between half-band width and brightness of disperse dyes on polyester is another matter.

From the molar extinction coefficient \((\epsilon_{\text{max}})\) data, dyes 5a and 5c seem to be more intensely absorbing than 5b, 5d and 5e. However, the true measure of tinctorial strength of dyes is obtained from the oscillator strength \((f)\), rather than \(\epsilon_{\text{max}}\). Since it expresses the area under the absorption curve (Eqn 1). This means that the dye with a high value but narrow absorption curve (i.e. low \(\Delta\nu_{\frac{1}{2}}\)) could be tinctorially weaker than the dye which although has a lower \(\epsilon_{\text{max}}\) value, has a broader
absorption curve (Karci, 2005).

\[ f = 4.32 \times 10^9 \times \Delta \nu_{3/2} \times \epsilon_{\text{max}} \ldots \]  

(1)

Thus, from Table 3, dye 5c gave high molar extinction coefficient but narrow absorption curve: Low \( \Delta \nu_{3/2} \), and so it is tintorially weaker than dyes 5a, 5b, 5d and 5e. These dyes, although have lower molar extinction coefficients, they have broader absorption curves and hence are tintorially stronger when compared with dye 5c.

CONCLUSION

A series of disazo dyes were synthesized from 2-methylphenol, 4-hydroxybenzoic acid, chromatropic acid, 4-aminophenol and 4-chloroaniline, as the coupling components, and 4-amino-3-nitrotoluene and 4-amino benzoeic acid as the carbocyclic diazo components. The solvent influence on the wavelength of maximum absorption was studied. It was observed that the absorption spectra of dyes 5a – e generally showed a maximum peak at longer wavelength in N,N-dimethylformamide and chloroform.

When compared with the absorption spectra of the dyes in ethanol, it was also observed that dyes 5a – d may exist as a mixture of tautomeric forms, in N,N-dimethylformamide. Dyes 5a, 5b, 5d and 5e can be applied to polyester and/or polyamide fibres as disperse dyes while dye 5c can only be applied to polyamide fibres due to the presence of acidic group.

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REFERENCES


