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Synthesis of Some New Azo Disperse Dyes and Investigation of Their Solvatochromic Effect

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ABSTRACT

The synthesis and properties of new monoazo dyes derived from the diazonium salts of p-amino benzoic acid , 3-trifluoromethyl aniline , 4-trifluoromethyl aniline are considered .The prepared compounds were characterized by UV-Visible , FT-IR and H NMR spectroscopic techniques . The effect of varying solvent upon the absorption ability of p-amino benzoic acid coupled with 4,4 –diethyl aniline , aniline ethanol , 2 – naphthol and 2,4 -dihydroxy benzene was examined .

Keywords: Mono and Bis Azodyes; Solvatochromic Effect ; P-Amino Benzoic Acid

INTRODUCTION

Azo compounds are the oldest and the most numerous class of commercial organic dyes. In this study, we synthesized a series of mono azo dyes on the basis of *p*-amino benzoic acid as diazotizing component and electron donating substituted aromatic compounds as coupling counter parts. Disperse (acidic or basic) dyes have found wide application in dyeing wool, polyamide fibers and blends of both these fibers [1]. These dyes are used in electrophotographic or sensor application for photoconductors [2].In addition, they are also preferred in high technology areas such as laser, electro-optical devices and ink-jet printers [3].

The present study focused on synthesis of azo dyes and the UV-Visible spectra of these dyes in different solvents (solvatochromic effect) were obtained. in different solvents (solvatochromic effect) were obtained. In continuation of our work we report here the synthesis of β-naphthol dyes.

The spectra characteristics of prepared compounds are reported. The compound structures are shown in Schemes 1 and 2.

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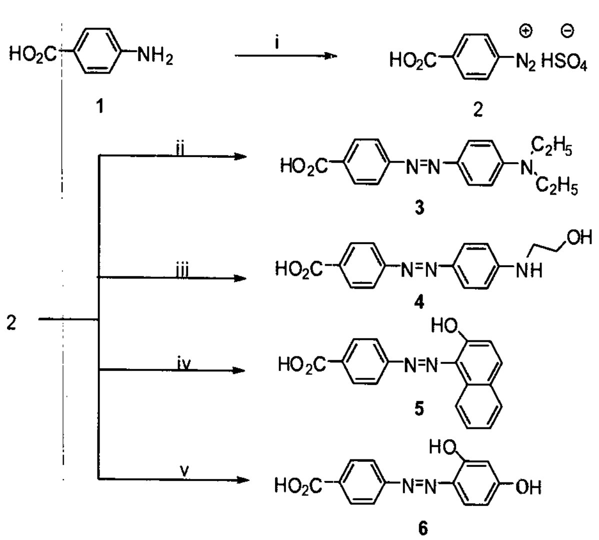
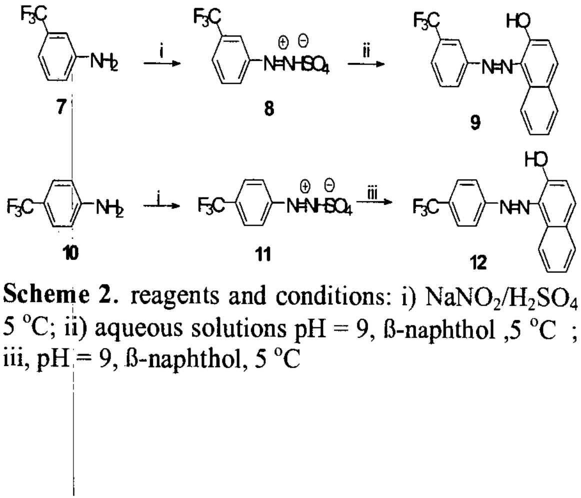


Scheme1. Reagents and conditions:i) NaNO2/H2SO4, 5°C, ii: Buffer (pH = 7) 5°C, C2H5OH, N,N-diethylaniline, iii: Buffer (pH=7) 5°C,C2H5OH, , iv: pH=9.5, 5°C, 2-(phenylamino)ethanol naphthalen-2-ol, v: pH=10,5°C, resorcinol.

In continution of our previous efforts, the monoazo chromophor group with CF_3 derivatives were synthesized and their properties were investigated [4,5]. We report here the synthesis of ß-naphthol dyes **5, 9, 12**. The compound, 1-(3-triflouromethyle-phenylazo)2-naphthol **9** and 1-(4-triflouromethyle-phenylazo)2-naphthol **12** were prepared by coupling.3-amino benzotriflourid **7** and 4-amino benzotriflourid **10** as diazonium salt with ß-naphthol in NaOH solution at pH = 9 (Scheme 2). As part of a continuing program to synthesize dyes and photochromism dyes which exhibit superior light and gas fastness [6,7], in this report azo dyes **9, 12** containing trifluoromethyl group have been prepared. Many of these dyes exhibit greater stability to light than their unfluorinated homologues [4,5].



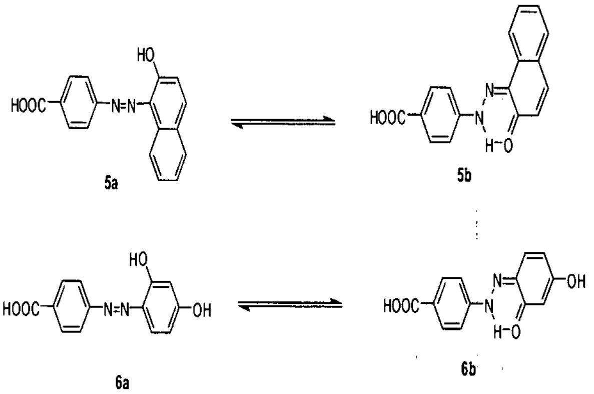
Scheme 2. reagents and conditions: i) $NaNO_2/H_2SO_4$ 5 °C; ii) aqueous solutions pH = 9, ß-naphthol ,5 °C ; iii, pH = 9, ß-naphthol, 5 °C

We found that the proper choice of diazonium and coupling constituents is necessary to obtain light-fast dyes. In general the gas fastness of fluorinated azo dyes was found to be excellent [8-12].

RESULTS AND DISCUSSION

Synthesis and Characterizations

The *p*-aminobenzoic acid dyes **3-6** were prepared by coupling *p*-aminobenzoic acid with aniline derivatives, ß-naphthol and resorsinol (Scheme 1). The dyes **5, 6, 9, 12** may exist in two possible toutomeric forms, namely the azohydrazone form A and B (ketohydrazone and hydroxyl azo) as shown in scheme 3. It can be suggested that dyes **5** , **6** are predominantly exist in the two tautomeric forms in all used solvents such as ; EtOH, CH_3CN, DMSO and CH_3COOH. Another dyes do not exist as the tautomeric form in solid state .Azodyes we studied are nonionic dyes, and appears to exist almost in its monomeric form at concentrations below about10^{-4}-10^{-5} M.We investigated **3, 4, 5, 6** Azodyes in different isotropic solvents (EtOH, CH_3CN, DMSO and CH_3COOH).It was observed that these solvents have strongly effect on the shift of λ_{max}.



Scheme 3.Toutomeric forms of compounds 5 and 6

The infrared spectra of 3-6 in KBr showed intense COOH acidic OH bands at 3200-3400 cm-1 and at 2534-3300 cm-1. It can be suggested that these dyes do not exist as the tautomeric form in solid state [8]. The IR spectra also show a band at 1500-1600 cm-1 ,which was assigned to azo (-N=N-) group. The IR spectra of 9 and 12 shows intense CF3 group at 1100-1200 cm-1. The other band of 3100-3053 cm-1 (aromatic C-H), 1600-1650 cm-1 (Ar C=C), 1676-1700 cm-1 (C=O) stretching band, 1240 cm-1 (C-O) stretching band. The 1H NMR spectra recorded in DMSO-d6 and DMSO 5%-CDCl3 at 25 °C using 500 MHz 1H NMR showed a singlet at 10.3-11.1 ppm for acidic hydrogen for dyes 3-6. These results show that the dyes 5-6 have a photochromic property and can exist as a mixture of toutomeric forms in DMSO.

SOLVATOCHROMIC EFFECT

UV-VIS absorption spectra were recorded in the wavelength range 350-600 nm. Absorption spectra of 3-6 were recorded in various solvents at a concentration of 10-4-10-5 M and these are all run at different concentrations [13]. The results are summarized in table1.The UV-VIS spectra of this dyes in different solvent (Solvatochromic Effect) were studied.

According to Bayliss and McRae, four limiting cases can be distinguished for intramolecular electronic transitions in solution.

(1) Nonpolar solute in a nonpolar solvent.
(2) Nonpolar solute in a polar solvent.
(3) Dipolar solute in a nonpolar solvent.
(4) Dipolar solute in a polar solvent.

In the present work we investigated the effect of isotropic solvent with the characteristic of (3) and (4) on the photophysical behaviors of Azodyes and shifts in the maximum of spectra was studied.The polarity and hydrogen bonding properties of the isotropic solvents used in this work, observed that have strongly effect on the λ_{max}.

Table 1. Influence of solvent on λ_{max} (nm) of dyes **3-6**

Dye no/λ_{max}	DMSO	acetic acid	acetonitril	ethanol
3	456	481	450	431
4	443	422	423	415
5	487	490	479	488
6	400	394	394	392

The dyes showed single absorbance's in various solvents except dyes **5** and **6**. Dyes **5** and **6** showed absorbance in all used solvents. It can be suggested that dyes **5** , **6** are predominantly exist in the two tautomeric forms in all used solvents such as; EtOH, CH_3CN, DMSO and CH_3COOH. It was observed that the absorption spectra of the dyes in acetic acid solvent predominantly involved bathochromically shifted. A typical example is shown in Figure 1 and 2. Dyes **5** and **6** were not changed significantly in all solvents due to the resonance in one ring.

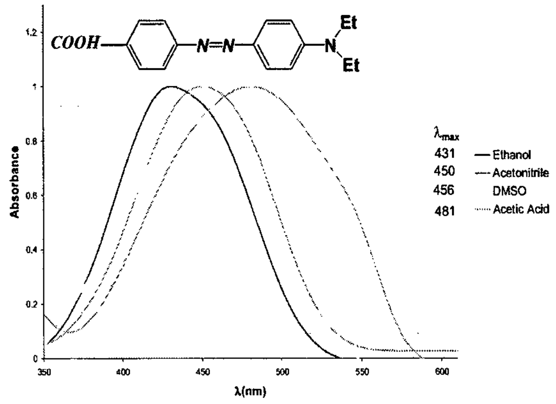


Fig.1. Absorption spectra of dye 3 in various solvents.

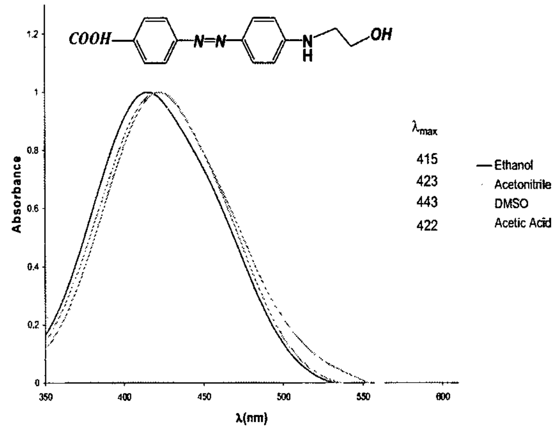


Fig.2. Absorption spectra of dye 4 in various solvents.

EXPERIMENTAL

The chemicals used in the synthesis of all dyes were obtained from Merck chemical company and were used without further purification. The solvents used were spectroscopic grade. IR spectra were recorded on a Shimadzo FT-IR 4100 in KBr. All NMR data were recorded Brucker Avance 500-MHz spectrometer ^1H NMR spectra were recorded in DMSO-d_6 and DMSO 5%-$CDCl_3$ with TMS as internal reference and chemical shifts are reported in ppm (δ). Absorption spectra were recorded on the UV/Vis and Diffuse Reflectance Spectra (DRS) using either Shimadzu UV-2100 equipped with an integrated sphere assembly or Carry 100 spectrophotometer in various solvents. All melting points are uncorrected and determined with a Metller FP_5 melting point apparatus.

4-((4-(diethylamino)phenyl)diazenyl)benzoic acid (3)

Prepared solution from Section 3.1 was gradually added to a solution of 0.48 ml (3mmol) N,N-diethy l aniline in 2 ml ethanol and 10 ml Buffer Solution prepared form acetic acid and sodium acetate in 5°C. After stirring for 1h, the progress of dye preparation was monitored by TLC the solvent system used was petroleum ether : EtOAc 5:2. The precipitated dye was isolated by filtration and washed with cooled water. Purification was achieved by recrystallization from 96% ethanol. The solid product **3** was collected by filtration and washed with water and recrystallized from ethanol / water, gives the 3 as light red crystals (0.89 g , 90 % yield), m.p : dec > 222°C ; IR (KBr) : ν 3300- 2534 (OH acid), 1679 (C=O), 1653 (C=C), 1596 (-N=N-), 1294 , 1247 (s), 757 (m) cm^{-1} ; ^{1}H NMR ($CDCl_3$ / DMSO 5 %) : δ ; 11.1 (s, 1 H, COOH), 8 (d , *J* = 8.3 Hz , 2H), 7.71 (d , *J* = 8.3 Hz , 2H) , 7.73 (d , *J* = 9 Hz , 2H), 6.6 (d , *J* = 9 Hz , 2 H), 3.3 (q , *J*= 7 Hz , 4 H , CH_2) , 1.1 (t , *J* = 7 Hz , 6 H, CH_3) ppm.

4-((4-(2-hydroxyethylamino) diazenyl) benzoic acid (4)

A similar procedure as used for 3 (section 3.3) was applied. Day **4** was obtained from *p*-aminobenzoicacid and 2 – anilinoethanol at buffer solution (recrystallized from Ethanol / Water) as orange crystals (0.62 g , 73 % yield) , m.p : dec >207 ; IR (KBr) : 3400 – 3200 (OH acid) , 2935 (NH), 2936 (Aliph – H), 1679 (C=O), 1600 (C=C), 1523 (–N=N–) , 1139 (C-N), 827 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$ / DMSO 5 %) : δ ; 10.3 (s, 1H , COOH), 7.9 (d , *J* = 8.4 Hz , 2 H), 7.6, (d , *J* = 8.4 Hz , 2 H), 7.6 (d , *J* = 8.9 Hz , 2 H), 6.5(d, , *J* = 8.9 Hz ,2 H), 5.3 (s, 1H) NH proton, 3.1 (t , *J* = 5.3 Hz , 2 H , CH_2) , 3.5 (t , *J* = 5.3 Hz , 2H , CH_2) , 1.8 (s, 1H , OH) ppm.

4-((2-hydroxynaphthalen)diazenyl)benzoic acid (5)

Dye **5** was obtained from *p* – amino benzoic acid and 2- naphthol at pH values of **9.5** as dark red powder (recrystalization from ethanol / water) (0.74 g, 85 5 yield) , m.p > 300 °C ; IR (KBr) : 3500 – 3000 (OH acid), 1676 (C=O) , 1600 , 1620 (C-O), 1502 (C=C), 1096 (w), 1137(m), 1149 (s), 840 (s) cm^{-1}.

4-((2,4-dihydroxyphenyl)diazenyl)benzoic acid (6)

Dye **6** was obtained from *p* – amino benzoic acid and 2,4 – dihydroxy benzene at pH values of 10 as brownish orange powder recrystallized from ethanol / water (0.63 g , 82 5 yield) , m.p > 270°c ; IR (KBr) : 3300 – 3000 (COOH), 1683 (C=O), 1600 (C=C) 1504 (–N=N–) , 1240 (C-O), 831 (s) cm^{-1} ; ^{1}H NMR ($CDCl_3$ / DMSO 5 %) : δ; 8 (d , *J* = 8.5 Hz , 2H , Ar .-H) , 7.7 (d , *J* = 8.5 Hz , 2H) , 7.6 (d , *J*= 9 Hz , 1H),6.5 (d , *J* = 9 Hz , 1H), 6.3 (s, 1H), 10(s, 1H , OH) , 13.7 (s, 1H , OH) ppm.

1–(3-trifluoromethyl–phenyl azo)2-naphthol (9)

This dye was obtained from 3 – trifluoro methyl aniline **7** and 2 – naphthol at pH values **9** as light orange with fluorescence brightness recrystallized from ethanol 96 %, 1.6 g , 90 % yield, m.p = 144-146 °C ; IR (KBr) : 3031 , 3062 (Ar.-H) , 1525 (C=O) , 1452 (–N=N-) ,1206 (w), 1251 (C-O), 1120 (CF_3) , 796 (m) cm^{-1} ; ^{1}H NMR($CDCl_3$) : δ ; 8 (s , 1H) , 7.9 (d , *J* = 8 Hz , 1H) ,7.47 (t , *J* = 8 Hz , 1 H) , 8.6 (d , *J* = 8 Hz , 1H , Ar.-H), 6.9 (d , *J* = 9.4 Hz , 1H) , 7.8 (d , *J* = 9.4 Hz , 1H) ,7.6 (m , *J* = 8 Hz , 3 H) , 7.5 (d , 1H , Ar.-H), 16.1 (s , 1H , OH) ppm.

1-(4-trifluoromethyl-phenylazo)2-naphthol (12)

This dye was obtained from 4- trifluoromethyl aniline **10** and 2- naphthol at pH values 9 as light orange crystal with fluorescence brightness recrystallized from ethanol 96 %, 0.54 g , 87 % yield) , m.p = 159-161 °C ; IR (KBr) : cm^{-1} 3053 (Ar.- CH) , 1616 (C=O) , 1562 (C=C) ,1504 (–N=N–) , 1256 (w) , 1325 (s) , 1107 , 1149 (CF_3) , 833 (s) cm^{-1}; ^{1}H NMR : 7.8 (m , *J* = 7.4 Hz , 4H , Ar.-H) , 6.81 (d , *J* = 8.4 Hz , 1H) , 8.5 (d , *J* = 8.4 Hz , 1 H) ,7.8 (m , 1H) ,7.45 (t , *J* = 7.4 Hz , 1H), 7.6 (m , *J* = 7.4 Hz , 2H), 7.6 (m, 1 H , naphthol ring) , 16.2 (s , 1 H , OH) ppm.

CONCLUSION

In this work, *p*-amino benzoic acid 1, *3*-trifluoromethyl aniline 7, 4-trifluoromethyl aniline10 and its dispers azo dyes have been synthesized .The UV-Visible spectra of this dyes in different solvent (Solvatochromic effect) were studied. Solvent effect plays an important role in photo-physical behavior of nonionic dyes,i.e.the intensity, shape, and maximum absorption wavelengths of the absorption bands of the nonionic dyes in solution depend strongly on the solvent-solute interactions and solvent nature.The solvent effect is closely related to the nature and degree of dye-solvent interactions.

The photophysical properties of the dyes are affected by the solvent nature as well as polarity.The solvatochromic behavior of dyes determined by is the shift of the absorption maximum wavelenght due to the presence of solvents with different polarity, which is due to the interaction between the solute and solvent molecules.

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REFERENCES

1. Bluss K, Dyes and Pigments., (1995) 41- 49.
2. B.R. Hsieh, Dyes and Pigments., 14 (1990) 287.
3. A.T. Peters and H.S. Freeman, Color Chemistry, Elsevier, 222Science, London., (1991) 286.
4. J.B. Dickey, E.B. Towne, S. Bloom, G.J. Taylor, H.R. Hill, 333R.A. Corbitt, M.A.McCall, W.H. Moore and D.G. 333Hedberg, Industrial and Engineering Chemistry., 45, (1953) 3331730.
5. American Association of Textile Chemists and Colorists, 333 443Technical Manual and Year .Book, Howes puplishing Co., 333 New York., 27 (1951)101.
6. N.O. Mahmoodi, H. Kiyani ,Bull. Korean Chem. Soc., 25 334(2004) 1417.
7. (a)N.O.Mahmoodi, M.A. Zanjanchi, H. Kiyani, J.Chem.Res., 44(2004) 438; (b) M.R. Yazdanbakhsh, N.O. Mahmoodi and 22Dabiry, Mendeleev Commun., (2006) 192.
8. American Association of Textile Chemist and Colorist, 222Technical Manual and Year.Book, Howes Publishing Co., 222New York ., 2 (1940) 194- 926.
9. American Association of Textile Chemist and Colorist, 222Technical Manual and Year.Book, Howes Publishing Co., 222New York., 2 (1950) 492- 972.
10. P. Scherer, Angew. Chem ., 52 (1923) 457.
11. S. Krishna, J. Chem Soc.,(1923) 156.
12. R. Kaminski, U. Lauk, P.Skrabal, H.Zollinger, Helv. Chim. 222 Acta., 66 (2002) 1983.
13. K. Fikret, D. Aykut, S. Izzet, T. Tahir, Dyes and Pigments., 222(2006) 91.