



Pelagia Research Library

Der Chemica Sinica, 2016, 7(2):93-100



Diazotization and coupling reactions of differently substituted aromatic amines and investigation of their solvatochromic behaviour

Neha and Manisha Patni*

Department of Chemistry, The IIS University, Jaipur, India

ABSTRACT

Prompted by the diverse applications of azo compounds, twenty four phenolic azo compounds have been synthesized and characterized by IR and ^1H NMR spectral techniques. The UV absorption maxima of each compound were determined in ethanol to investigate the substituent effect in the synthesized compounds. It was found that electron releasing group produced maximum bathochromic shift. To understand the effect of solvent on absorption maxima, the behaviour of three representative azo compounds (3b, 7b and 8b) was also investigated in eight solvents having a variety of polarity, it was observed that the highest polar solvent produced maximum bathochromic shift in all cases.

Key words: Azo compounds, Absorption maxima, Substituent effect, Solvent effect

INTRODUCTION

Azo dyes are important class of organic compounds consisting of at least one conjugated azo ($-\text{N}=\text{N}-$) group as chromophore. This chromophoric moiety may be associated with two or more aromatic or heterocyclic rings to enhance the color. There may be more than one azo group present in the dye molecules and thus classified into monoazo, diazo, triazo, and so on according to the number of azo moieties present in the molecule [1]. Azo group is characterized by the presence of an orbital containing a lone pair on each nitrogen atom. Majority of these compounds are derived from the coupling of diazotized amines with aromatic hydroxyl and amino compounds.

Azo compounds constitute an important class in organic synthesis as they are used as precursors for the synthesis of variety of organic compounds containing nitrogen or sulfur moieties [2-6]. This type of molecules have diverse applications. They are used not only as classical synthetic dyes and pigments, but also as solvatochromic probes and thermally stable organic second-order nonlinear optical (NLO) chromophores [7-10]. Due to its excellent thermal and photochemical properties, these groups are also used as optical data storage, photo switching and holography materials. Polymers with azo units are also reported as promising candidates for photoactive materials [11-12].

The azo group is photochromic, redox responsive, pH-sensitive and stabilizes low valent metal oxidation states due to the presence of a low-lying azo centered π^* - molecular orbital. The azo compounds are used as metal ion indicator in acid-base and complexometric titration. Also, they are used as daylight fluorescent pigments and laser dyes due to their excellent color characteristics and high photostability [13-14]. Azo dyes are currently used in abundance as dyes and pigments in textile industry [15-17] and other industries such as leather, plastics, cosmetics and food materials [18-19].

Azo compounds are also involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and biological activity against bacteria and fungi [20-21]. They show herbicidal, anti-inflammatory, anti-microbial or antiparasitic, antiulcer, antifungal, antibacterial, antitubercular, antidiabetics, antiseptics, antibiotic and other chemotherapeutic activities [22-26].

The azo compounds possess suitable binding characteristics due to the presence of $-N=N-$ group and a variety of metal complexes with transition metal ions are reported with unusual structural and magnetic properties [27-29].

The success of azo colorant is due to the simplicity of their synthesis by diazotization and azo coupling, almost innumerable possibilities are reported by variation of the diazo and coupling components [1]. Phenolic azo dyes have several advantages over other commercial dyes including their wide color range, good color fastness and ability to absorb light. These groups are also known as matrix resins or binding resins for various applications, easy availability and excellent properties such as high thermal binding stability, excellent acid resistance, high fire retardancy, etc [30]. Naphthols are also reported to be used as well-established intermediates for the synthesis of dyes [31]. They can also be synthesized cheaply because the starting materials are readily available, inexpensive compounds; most of the chemistry is completed at or below room temperature; and the environmental impact is low due to the use of water as a solvent in all the reactions.

Brief review of literature reported above shows that the diazo group confers interesting chemical and biological properties to the amino derivatives. In this view, the reactivity of some aromatic amines has been explored towards diazotization and further coupling with a variety of coupling components like phenols, resorcinol and naphthol. The synthesized azo compounds were purified and characterized by analytical methods, like IR and ^1H NMR spectroscopy. The UV absorption studies of several products were also carried out in organic solvents of different polarity at room temperature to understand the nature of interaction of the chromophore group with the different amino compounds and identify their potential photochemical applications [32-33].

MATERIALS AND METHODS

Materials & Instruments

All reagents and chemicals were of commercial grade and used without further purification. Solvents were dried using literature method [35]. Melting points ($^{\circ}\text{C}$) were measured in open glass capillaries using electric melting point apparatus and are uncorrected. Shimadzu IR spectrophotometer was used for recording the IR spectra of the synthesized compounds using KBr pellets in the range between $4000-200\text{ cm}^{-1}$. ^1H NMR spectra were recorded on Joel EX-400 MHz spectrometer (observation frequency 399.6) in CDCl_3 -DMSO- d_6 (5 mm tube) using tetramethylsilane (TMS) as an internal standard. The UV-vis absorption spectra were measured using a Shimadzu UV-1800 spectrophotometer. Purity of the final product was checked by TLC using silica gel plate and visualization with Iodine chamber.

Synthesis of azo compounds of differently substituted amino compounds

The twenty four azo compounds were prepared by diazotization of differently substituted anilines (**1a-d**) followed by coupling with electron rich aromatic compounds i.e. phenols, resorcinol and naphthol (Scheme 1). The reaction has been carried out as follows-

To **1a-d** [0.01 mol] was added HCl (0.01 mol, 0.37 g, 0.73 ml, 50% aqueous solution) and stirred well and cooled to 0°C in an ice-bath. To the resulting slurry was added an aqueous solution of NaNO_2 (0.01 mol, 0.69 g in 10 ml distilled water) drop wise with vigorous stirring. The temperature of the solution was kept between 0° and 5°C . A clear solution of diazonium salt (**2a-d**) was obtained, which was again stirred for 5-10 min. and used for the coupling reaction in situ.

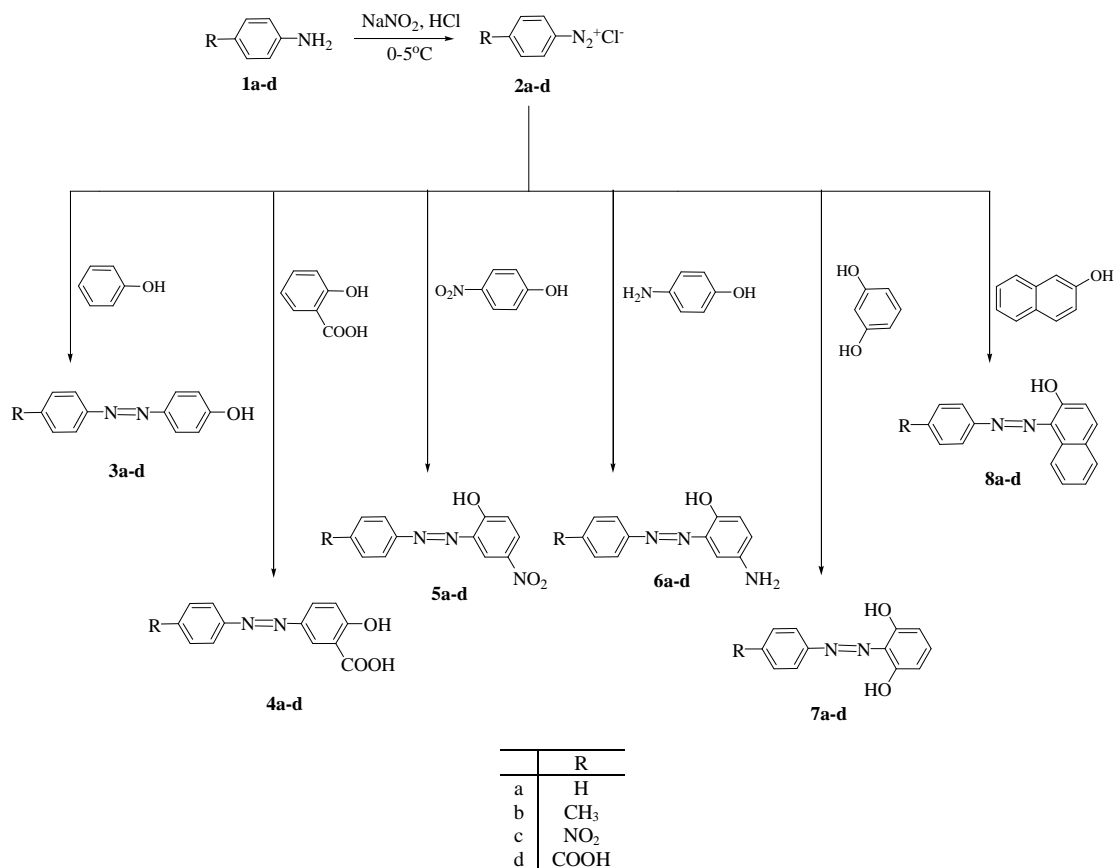
To the 0.01 mol solution of individual couplers was added NaOH (2.5 mol, 5 g in 50 ml distilled water) and cooled in an ice-bath. The temperature was maintained between $0-5^{\circ}\text{C}$. To the solution of diazonium salt of the amines (**2a-d**) prepared earlier, solution of individual coupler was added slowly with constant stirring. The azo compound formed as a reaction of **2a-d** with individual coupling reagent, was separated out in the form of precipitate. For complete precipitation pH of the reaction mixture was maintained at 6 using dil. NaOH. The reaction mixture was further stirred for one hour in ice-bath and kept overnight at room temperature. The resulting azo compound was

filtered, dried and recrystallized from ethanol. The synthesized compounds were characterized by UV, IR and ^1H NMR spectral techniques.

RESULTS AND DISCUSSION

Synthesis of new azo compounds of differently substituted aromatic amines

A variety of twenty four azo compounds have been synthesized via diazotization and coupling reactions of differently substituted amines with several coupling components i.e. phenols, resorcinol and β -naphthol using reported methods [34]. (Scheme 1)



Scheme 1: Synthesis of new azo compounds from the reaction of differently substituted aromatic amines with phenol and its derivatives, resorcinol and β -naphthol

The azo compounds thus obtained are stable and crystalline solids and soluble in ethanol, methanol, chloroform, dimethyl sulfoxide and *N,N*-dimethylformamide but insoluble in non polar solvents such as benzene, n-hexane and carbon tetrachloride. Brilliant hues from dark brown to red are observed. Sharp melting points were not observed and they decomposed above 200°C. The synthesized compounds were characterized by IR and ^1H NMR spectral techniques. The physical data of these synthesized compounds are presented in Table 1.

Table 1: Physical data of synthesized azo compounds

Compound	M.F.	M.Wt.	Yield (%)	Color
3a	C ₁₂ H ₁₄ N ₂ O	198	62	Yellow orange
3b	C ₁₃ H ₁₆ N ₂ O	212	65	Yellow orange
3c	C ₁₂ H ₁₃ N ₃ O ₃	243	58	Dark red
3d	C ₁₂ H ₁₃ N ₂ O	242	58	Red
4a	C ₁₃ H ₁₅ N ₂ O	247	78	Orange
4b	C ₁₄ H ₁₇ N ₂ O ₃	261	63	Red
4c	C ₁₃ H ₁₄ N ₃ O	292	65	Red
4d	C ₁₄ H ₁₅ N ₂ O ₃	259	71	Red
5a	C ₁₂ H ₁₄ N ₃ O ₃	248	53	Yellow orange
5b	C ₁₃ H ₁₆ N ₃ O ₃	262	63	Dark red
5c	C ₁₂ H ₁₃ N ₄ O ₅	293	55	Orange
5d	C ₁₃ H ₁₄ N ₃ O ₅	292	61	Red
6a	C ₁₂ H ₁₆ N ₃ O	218	67	Dark red
6b	C ₁₃ H ₁₈ N ₃ O	232	70	Orange
6c	C ₁₂ H ₁₅ N ₄ O ₃	273	52	Red
6d	C ₁₃ H ₁₆ N ₃ O ₃	262	58	Brick red
7a	C ₁₂ H ₁₄ N ₂ O ₂	214	64	Orange
7b	C ₁₃ H ₁₆ N ₂ O ₂	228	69	Dark orange
7c	C ₁₂ H ₁₃ N ₃ O ₄	259	68	Dark red
7d	C ₁₂ H ₁₃ N ₂ O ₂	258	70	Red
8a	C ₁₆ H ₁₆ N ₂ O	248	62	Dark red
8b	C ₁₇ H ₁₈ N ₂ O	262	56	Dark red
8c	C ₁₆ H ₁₅ N ₃ O ₃	293	66	Dark brown
8d	C ₁₆ H ₁₇ N ₂ O	292	58	Dark brown

Characterization of azo compounds synthesized in section 2.1

IR Spectra

The IR spectra of all the compounds have been recorded in KBr. The appearance of N=N- stretching peak in the range 1400-1510 cm⁻¹, aromatic C-H stretching in the range 3100-3280 cm⁻¹ and O-H stretching (broad) in the range 3000-3350 cm⁻¹ in all synthesized compounds confirmed the formation of azo bond, presence of aromatic ring and OH group respectively. The presence of methyl group in compounds **3b-8b** resulted in a characteristic C-H stretching and C-H bending absorption in the range 2960-2800 cm⁻¹ and 1400-1300 cm⁻¹ respectively. A peak in the range 1510-1380 cm⁻¹ corresponds to N-O stretching confirmed the presence of NO₂ group in compounds **3c-8c**, **5a**, **5b** and **5d**. A sharp peak in the range 1740-1700 cm⁻¹ and 1250-1150 cm⁻¹ corresponds to C=O and C-O in carboxylic acids has also been observed in **3d-8d** and **4a-4c**. Presence of NH₂ group in **6a-d** due to the coupling agent showed peak in the range 3250-3380 cm⁻¹.

¹H NMR Spectra

The ¹H NMR spectra of all compounds were recorded in a mixture of CDCl₃ and DMSO-d₆ solvent. All compounds exhibited an unresolved multiplet in the range δ6.3 - 8.2 corresponding to phenyl and aryl group present. A broad peak in the range δ4.7-5.1 corresponding to -OH group is also observed in all compounds. A broad peak in the range δ4.6-4.8 corresponding to NH₂ protons is also exhibited in **6a-d**. Presence of CH₃ group in **3b-8b** showed a singlet at δ2.35 corresponding to three protons respectively. Presence of COOH group in compounds **3d-8d** and **4a-4c** is also confirmed by the presence of a sharp signal at δ11.0-12.0.

Investigation of solvatochromic behaviour of diazonium coupling products

To investigate the absorption maxima of synthesized azo compounds, the absorption spectra of all compounds was recorded in ethanol at concentration of 10⁻⁵ mol dm⁻¹ over the λ range 400 – 800 nm. Effect of changing the substituent in diazo compound on λ_{max} value has also been investigated. The results are presented in Table 2.

λ_{max} Values presented in Table 2 indicated that the position of the UV absorption maxima changes with the nature of the substituent on the diazo group as well as the coupling component. Presence of electron releasing group in coupling component in all compounds produced bathochromic shift in the range of 30-40 nm in comparison to their diazo component. It was found that highest bathochromic shift is shown by **7a-7d**, which may be attributed to the more electron releasing capacity of resorcinol in comparison of phenol. Presence of β-naphthol ring exhibited a comparatively lesser red shift.

Table 2: UV absorption maxima of azo compounds in ethanol

Compound	Diazo compound	Coupling component	λ_{max} (in nm)
3a	Aniline	Phenol	410
3b	<i>p</i> -Toluidine	Phenol	440
3c	<i>p</i> -Nitro aniline	Phenol	400
3d	<i>p</i> -Amino benzoic acid	Phenol	430
4a	Aniline	Salicylic acid	405
4b	<i>p</i> -Toluidine	Salicylic acid	435
4c	<i>p</i> -Nitro aniline	Salicylic acid	395
4d	<i>p</i> -Amino benzoic acid	Salicylic acid	415
5a	Aniline	<i>p</i> -Nitro phenol	400
5b	<i>p</i> -Toluidine	<i>p</i> -Nitro phenol	420
5c	<i>p</i> -Nitro aniline	<i>p</i> -Nitro phenol	390
5d	<i>p</i> -Amino benzoic acid	<i>p</i> -Nitro phenol	410
6a	Aniline	<i>p</i> -Amino phenol	415
6b	<i>p</i> -Toluidine	<i>p</i> -Amino phenol	445
6c	<i>p</i> -Nitro aniline	<i>p</i> -Amino phenol	410
6d	<i>p</i> -Amino benzoic acid	<i>p</i> -Amino phenol	425
7a	Aniline	Resorcinol	496
7b	<i>p</i> -Toluidine	Resorcinol	513
7c	<i>p</i> -Nitro aniline	Resorcinol	490
7d	<i>p</i> -Amino benzoic acid	Resorcinol	504
8a	Aniline	β -Naphthol	490
8b	<i>p</i> -Toluidine	β -Naphthol	503
8c	<i>p</i> -Nitro aniline	β -Naphthol	480
8d	<i>p</i> -Amino benzoic acid	β -Naphthol	494

Table 3: UV absorption data of 3b, 7b and 8b in different organic solvents

S. No.	Solvent	3b	7b	8b
1.	n-Hexane	415	498	490
2.	Benzene	415	500	490
3.	Methylene chloride	430	510	498
4.	Ethanol	440	513	503
5.	Chloroform	435	510	500
6.	Acetonitrile	430	510	500
7.	Dimethylformamide	445	535	525
8.	Dimethyl sulfoxide	450	535	528

To investigate the solvatochromic behaviour of the coupling products, the absorption maxima of three representative compounds **3b**, **7b** and **8b** has been investigated in variety of protic and aprotic solvents- n-hexane, benzene, methylene chloride, ethanol, chloroform, acetonitrile, dimethylformamide and dimethyl sulfoxide. The concentration (10^{-5}) and λ range (400 – 800 nm) was kept same while studying the effect of solvent. The UV absorption maxima of these azo compounds in various organic solvents are given in Table 3 and also presented in Figure 1, 2 and 3 respectively.

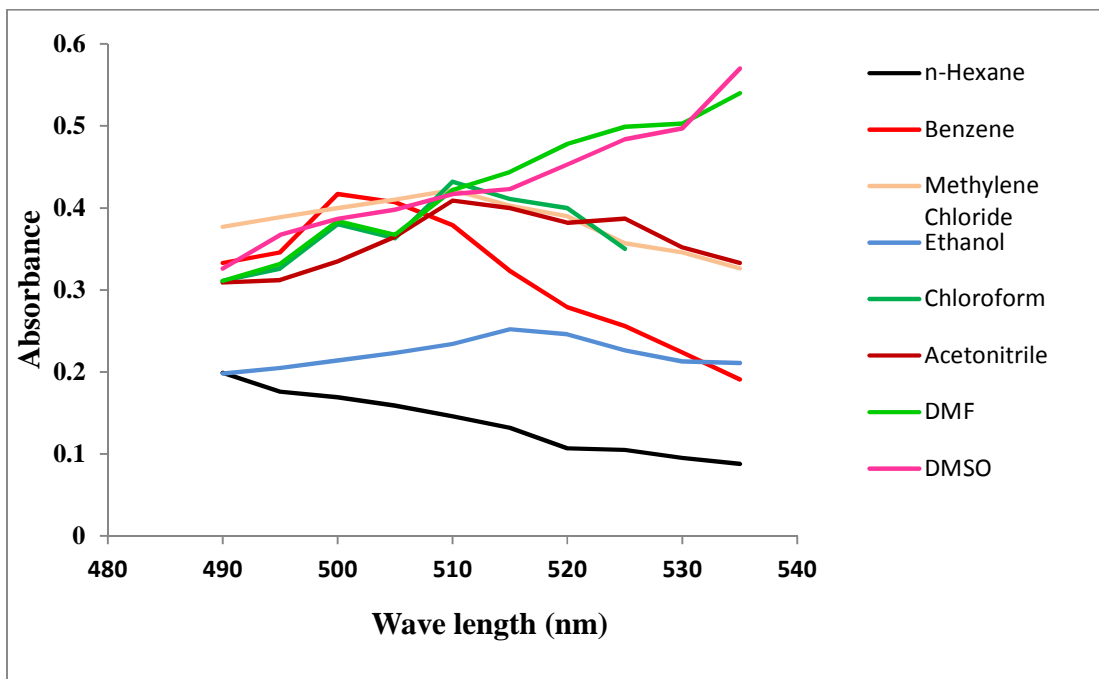


Figure 1: UV absorption maxima of 3b in solvents of different polarity

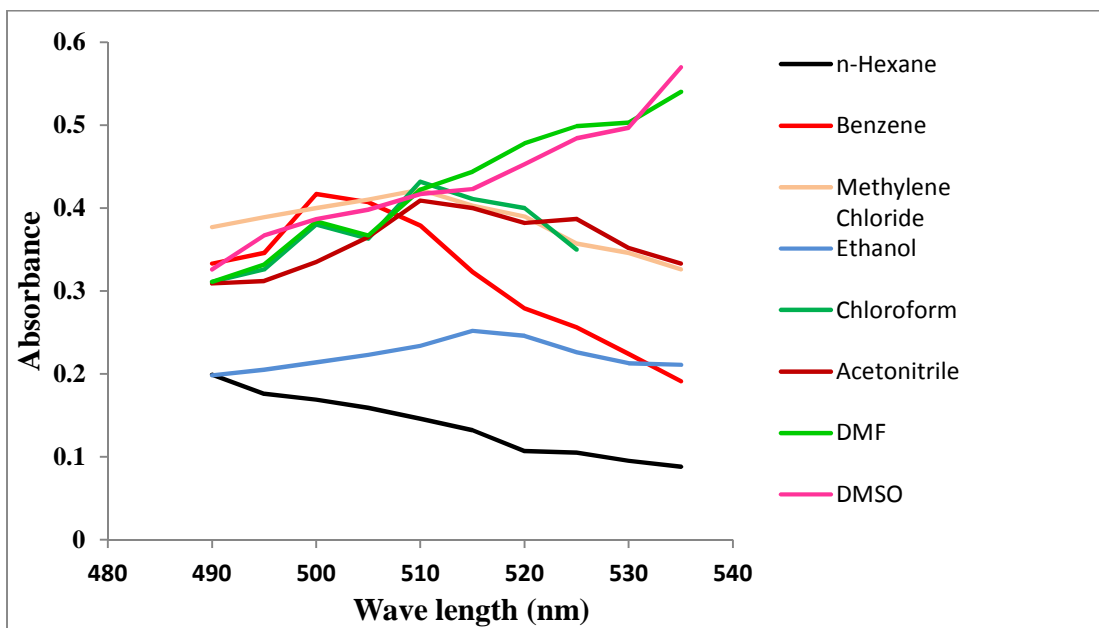


Figure 2: UV absorption maxima of 7b in solvents of different polarity

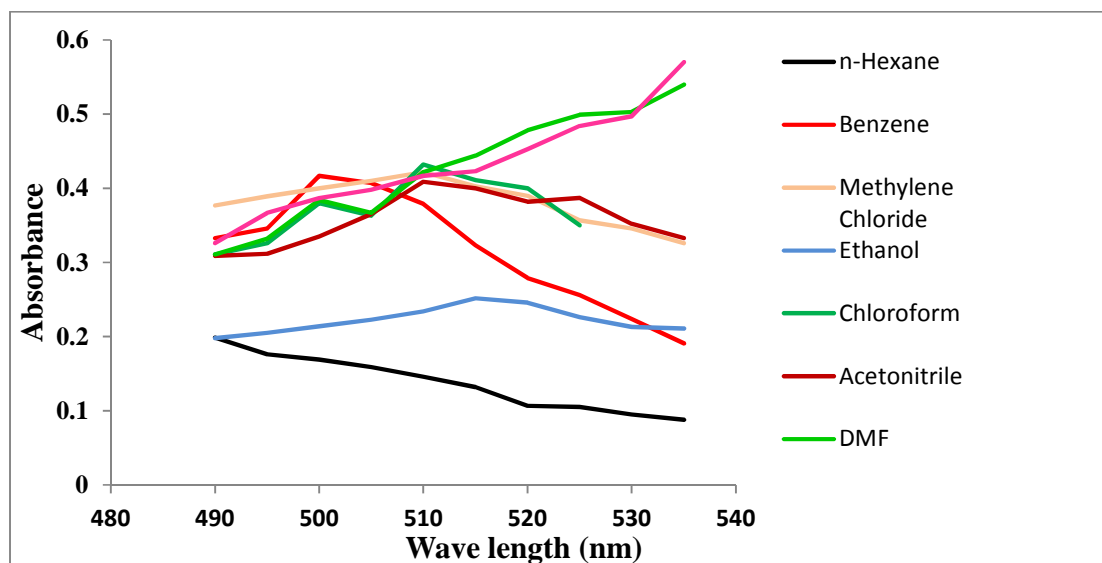


Figure 3: UV absorption maxima of 8b in solvents of different polarity

It was found that the absorption maxima of these compounds are strongly solvent dependent and vary with solvent polarity. These compounds generally showed bathochromic shift as the polarity of the solvents was increased. It was found in all the cases that although in ethanol, chloroform and acetonitrile, the absorption spectra of the compounds did not change significantly, the λ_{\max} of the compounds shifted considerably in DMF and DMSO.

CONCLUSION

A variety of twenty four azo compounds have been synthesized via diazotization and coupling reactions of differently substituted aromatic amines with several coupling components. The synthesized azo compounds were characterized by IR and ^1H NMR spectroscopy. The absorption maxima and solvatochromic behaviour of some representative azo compounds has also been investigated.

REFERENCES

- [1] P. K. Santra, D. Das, T. K. Misra, R. Roy, C. Sinha, S. M. Peng, *Polyhedron*, **1999**,18,1909.
- [2] H. Karear, I. E. Gumerukcuoglu, *Turk. J. Chem.* **1999**,23,67.
- [3] A. A. Jarrahpour, M. Zarei, *Molbank*, **2004**,M376,1.
- [4] J. P. Li, P. Liu, Y. L. Wang, *Chin. Chem. Lett.* **2003**,14,677.
- [5] M. C. Sharma, D. V. Kohli, S. Sharma, A. D. Sharma, *Der Pharmacia Sinica*, **2010**,1,124.
- [6] S. Gopalakrishnan, N. T. Nevadith, C. V. Mythili, *Der Pharmacia Sinica*, **2011**,2,138.
- [7] R. S. Abramov, D. L. Bankoort, *J. Phys. Chem.* **1993**,31,23.
- [8] A. Takadate, T. Masuda, C. Murata, A. Isobe, T. Shinohara, M. Irikura, S. Goya, *Anal. Sci.* **1997**,13,753.
- [9] C. H. Chen, J. Shi, *Coord. Chem. Rev.* **1998**,171,161.
- [10] S. Wu, W. Quin, Z. Xia, Y. Zou, S. Wang, S. Shen, *Chem. Physica Lett.* **2000**,5,535.
- [11] H. Faustino, M. Reda, P. Almeida, P. F. Santos, *Tetrahedron Lett.* **2008**,49,6907.
- [12] M. He, Y. Zhou, R. Liu, J. Dai, Y. Cui, T. Zhang, *Dyes Pigm.* **2009**,80,6.
- [13] J. O. Otutu, *Oriental J. Chem.* **2012**,28,787.
- [14] E. H. Shahinian, I. Haiduc, I. Sebe, *Sci. Bull. Series B* **2011**,73,153.
- [15] K. Gharanjig, M. Arami, S. Rouhani, H. Bahrami, B. Movassagh, N. M. Mahmoodi, *J. Chin. Chem. Soc.* **2007**,54,1021.
- [16] S. J. Naik, U. P. Halkar, *Arkivoc*, **2005**,13,141.
- [17] A. Khosravi, S. Moradian, K. Gharanjig, A. Taorami, *J. Chin. Chem. Soc.* **2005**,52,495.
- [18] H. Song, K. Chen, D. Wu, H. Tian, *Dyes Pigm.* **2004**,60,111.
- [19] H. Hartman, M. Schulze, *Dyes Pigm.* **1991**,15,255.

-
- [20] A. S. Alimmari, A. D. Marinkovic, D. Z. Mijin, N. V. Valentic, N. Todorovic, G. S. Uscumlic, *J. Serb. Chem. Soc.* **2010**,75,1019.
- [21] A. M. Khedr, M. Gaber, R. M. Issa, H. Erten, *Dyes Pigm.* **2005**,2,475.
- [22] E. Tajouri, M. M. El-ajaili, M. A. Abuzveda, H. F. El-amary, E. S. Ahmed, *J. Asic. App. Sci.* **2005**,15,41.
- [23] K. M. Mistry, K. R. Desai, *E-J. Chem.* **2004**,1,189.
- [24] K. H. Patel, *E-J. Chem.* **2006**,3,103.
- [25] M. T. Shreenivas, B. P. Chetan, A. R. Bhat, *J. Pharma. Sci. Technol.* **2009**,1,88.
- [26] A. Gursoy, N. Terzioglu, *Turk. J. Chem.* **2005**,29,247.
- [27] A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman, R. D. Rogers, *Sep. Sci. Technol.* **2001**,36,785.
- [28] J. Peng, C. Deng, S. Liu, *Fenxi Huaxue*, **1998**,26,303.
- [29] D. S. Sigman, D. R. Graham, V. D. Aurora, *J. Biol. Chem.* **1979**,254,1269.
- [30] P. C. Tsai, I. J. Wang, *Dyes Pigm.* **2007**,74,578.
- [31] V. R. Kanetkar, R. R. Walavalkar, *J. Serb. Chem. Soc.* **2005**,70,1249.
- [32] S. Fozooni, A. M. Tikdari, H. Hamidian, H. Khabazzadeh, *Arkivoc* **2008**,14,115.
- [33] A. K. Singh, S. Kanvah, *J. Chem. Soc., Perkin Trans.* **2001**,2,395.
- [34] V. H. Patel, M. P. Patel, R. G. Patel, *Dyes Pigm.* **2002**,52,191.
- [35] B. S. Furniss, A. J. Hannaford, P.W.G. Smith, A. R. Tatchell, *Vogel's Text Book of Organic Chemistry*, Pearson Education, **2007**.