Original Research Paper

Volume-8 | Issue-2 | February-2018 | PRINT ISSN No 2249-555X

Chemistry

COMPARATIVE STUDY OF AZO COMPOUNDS CONTAINING ALDEHYDE MOIETY BASED ON THE CHARACTERISATION AND ANTIMIROBIAL ACTIVITY

Ms.T.Swarna Karthika* — Assistant Professor, Department of Chemistry and SDNB Vaishnav College for Women, Chrompet, Chennai-44. *Corresponding Author

Dr. (Mrs).C. Mansiya — Assistant Professor and Head, Department of Chemistry &, SDNB Vaishnav College for Women, Chrompet, Chennai-44.

ABSTRACT A comparative study of azo compounds, characterized by spectral techniques and antimicrobial activity. Azo dyes have been synthesized using substituted aromatic amines and various Aldehydic compounds by using diazotization reaction followed by coupling reaction.. The resulting dyes were characterized by spectral techniques like UV, IR, H1-NMR and screened for the antimicrobial activities against five different bacterial species.

KEYWORDS : Azo compounds, Antimicrobial activity, IR, NMR.

Introduction:

Azo compounds, with two phenyl rings separated by an azo (-N=–) bond are versatile molecules and have received much interest in research areas, both fundamental and application[1-3]. Colorants, which include chromo-phores of dyes usually consisting of C=C, N=N, C=N, and aromatic and heterocyclic rings, containing oxygen, nitrogen or sulfur, have been widely used as dyes owing to their versatility in various fields and high technologies including paper, leather, plastics, biological staining, lasers, liquid crystalline displays, ink-jet printers, and in specialized applications such as food, drug, cosmetic and photochemical productions, Azo compounds are very important molecules and have attracted much attention in academic and applied research [4-7]. Dyes used before nineteenth century were either of vegetable (i.e., weld, madder, indigo) or animal origin (i.e., cochineal, shellfish) and belonged to various chemical types such as flavonoids (yellow), anthraquinones (red) and indigoids (blue and violet). Azo dyes are widely used in the textile industry and are the largest and most versatile group of synthetic organic dyes with a tremendous number of industrial applications [8-9]. Azo dyes are the most essential class of commercial dyes. the azo group is photochromic, redox responsive, pH-sensitive, stabilizes low valent metal oxidation states due to the presence of a low-lying azo centered π* molecular orbital. It is used as a metal ion indicator in complexometric titration[10-14]. They are highly coloured and possesses excellent thermal and optical properties and shows important applications such as optical data storage, photo switching and nonlinear optical materials [15-18]. They are involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and biological activity against bacteria and fungi. The azo compounds are highly colored and have been used as dyes and pigments [19-21]. In the field of azo dyes, phenolic compounds play a major role for synthesizing most of the commercial dyes. Most of the dyes are marketed in the form of azo disperse, azo-vat, azo-acid dyes, etc. Most of these commercially available dyes have the naphthols bearing hydroxyl groups as an auxochrome group. Azo compounds have received much attention due to their versatile use in many practical applications such as coloring fiber, photoelectronic applications, printing systems, optical storage technology and in various analytical techniques.[22] The azo compounds also find their wide applications as a polymer additive.[23-24] The uses of dyes in the various industrial field shows that azo compounds are the largest class of industrial synthesized organic dyes. Azo dyes are well known for antiseptic activity [25-26] and some are useful as chemotherapeutic agents [27].Transition metals like Fe, Co, Ag, Au, Cu and Ni have long been used in medicine[28-30]. There are about 3000 azo dyes currently in use all over the world. Although some azo dyes have been reported to be toxic, dozens of additional monoazo dyes are permitted in drugs and cosmetics[31-32]. The azo dyes posses antiseptic and antiprotozoal properties and also promote wound healing. The cationic dyes are more active in acidic medium and preferably attack on gram positive bacteria as compared to anionic dyes. Most common azo dyes used as antiseptics are scarlet red & diamazon[33]. The medicinal properties of azo compounds particularly synthesized from acetyl salicylic acid, thymol, aldimine and -napthol etc. have been frequently reported[34].

Experimental method:

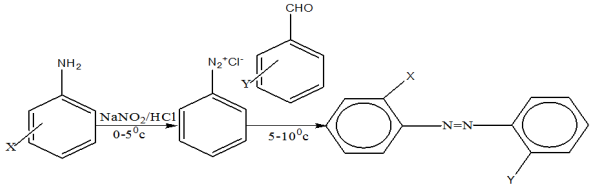
All the chemicals and solvents were obtained from Merck Company Ltd (AR-Grade). UV-spectra were recorded using the Instrument Elico. FT-IR-spectra were recorded using a Perkin Elmer Instrument. H^1-NMR spectra of the synthesized azo compounds were recorded using Aspeet spectrometer using DMSO solvent and TMS as the internal standard. The antimicrobial activity of azo dyes was analyzed in micro lab Chennai.

General procedure for synthesis of azo compounds:

Substituted aromatic amine (15 mmol) is treated with 5ml of con HCl and 5ml cold solution of sodium nitrite was added with constant stirring. The temperature of the reaction was maintained upto 0-5^{0}C. Diazonium salt solution prepared was added drop wise to substituted aldehydic compounds (15mmol). The reaction mixture stirred for about 10-30 minutes maintaining the temperature between 5-10^{0}C. The colored product obtained is filtered and washed with water. The product synthesized was recrystallized using ethanol.

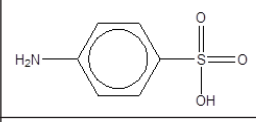
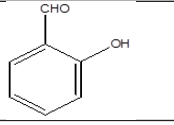
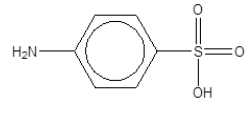
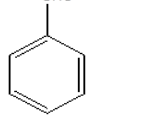
Results and Discussion

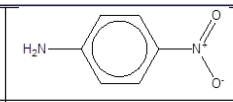
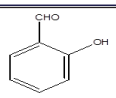
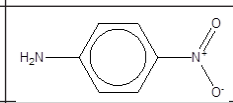
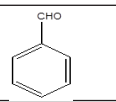
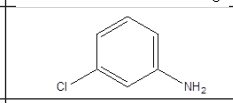
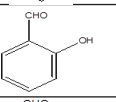
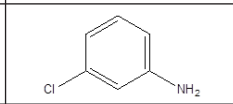
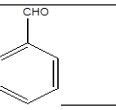
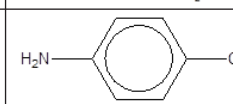
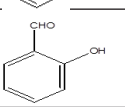
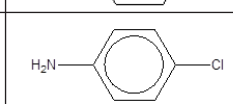
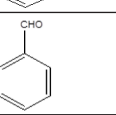
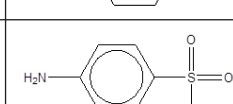
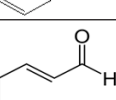
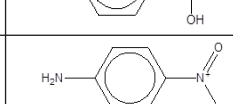
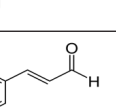
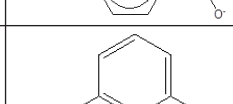
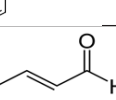
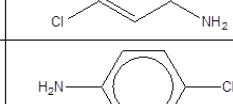
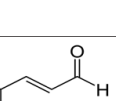
The azo compounds with various substituents were synthesized by diazotization reaction of various substituted aromatic amines followed by coupling reaction with substituted aldehydic compounds (Scheme-1.Sulphanilicacid, m-nitroaniline, p-chloroaniline and m-chloroaniline were diazotized and coupled with aldehydic compounds such as Salicylaldehyde, Benzaldehyde and Cinnamaldehyde. The product azo dye obtained was recrystallised using ethanol. The substituted aromatic amines and aldehydic compounds used for the synthesis of azo dyes were given in Table-1.



Scheme-1

TABLE-1 PREPARATIVE DETAILS OF AZO DYES

S.NO	AROMATIC AMINES	ALDEHYDIC COMPOUND
1.		
2.		

3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		

UV-Vis Absorption Spectra

Typical characteristic UV-Vis absorption bands of Azo dyes in DMSO are given in **Table-2**

Table 2 (UV-Vis absorption bands of Azo dyes in DMSO)

S.NO	COMPOUND	π - π*
1	1	390.9
2	2	393.9
3	3	393.7
4	4	388.7
5	5	387.0
6	6	390.5
7	7	391.6
8	8	392.6
9	9	388.8
10	10	394.5
11	11	389.1
12	12	389.9

IR-Absorption bands

IR spectrum of the dyes were recorded in the FT–IR spectrometer . It shows characteristic bands which are located at about the range of expected signals which corresponds to various groups present in each compounds . The characteristic IR absorption band of azo group N=N is located at 1400-1600cm-[1] The -O-H stretching frequency is from 3400-3600cm-[1]and the sulphonyl group frequency is at 1160-1180cm-[1]. The C=C aromatic frequency at 1500-1700cm-[1] .

Table -3 shows characterstic IR- Absorption bands.

Table 3 (Characteristic IR-absorption bands of azo dyes)

Compound	OH	N=N	C=O	C-O
1	3384	1483	1657	1195
2	3488	1486	1590	1165
3	3154	1344	1618	1194
4	3284	1347	1522	1247
5	3395	1461	1568	1187
6	3192	1447	1590	1240
7	2917	1483	1608	1183
8	3067	1483	1622	1190
9	3463	1404	1632	1108
10	3585	1344	1615	1197
11	3145	1451	1579	1154
12	3035	1479	1586	1158

NMR investigations

In their 1H NMR spectra, all azo compounds show a peak at 9–10. ppm, belonging to the aldehydic group.1H NMR spectra of azo compounds show peaks at 8.11–8.20 ppm, ,7.14–7.22 ppm and at 8.01–8.1 ppm, which are attributed to phenyl group including aldehydic group. Table -4

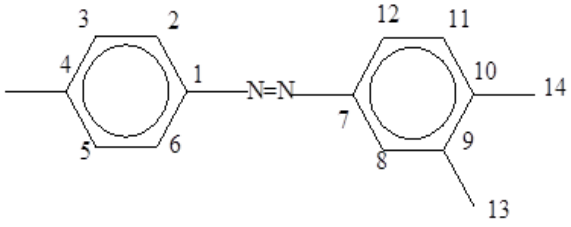


Table-4 H[1]-NMR signals of Azo compounds

	1	2	3	4	5	6	7	8	9	10	11	12
H[2]	6.690 (d)	6.975 (d)	6.996 (d)	7.462 (t)	6.996 (t)	7.222 (d)	6.570 (d)	6.563 (d)	6.478 (d)	6.555 (d)	7.138 (d)	6.560 (t)
H[3]	6.982 (d)	6.992 (d)	7.011 (t)	7.477 (d)	7.337 (t)	7.380 (d)	6.988 (d)	7.110 (d)	6.998 (d)	7.014 (d)	7.187 (d)	7.006 (t)
H[4]	7.208 (d)	7.450 (t)	7.377 (d)	7.552 (d)	7.364 (d)	7.416 (d)	7.004 (d)	7.298 (d)	7.100 (d)	7.273 (d)	7.337 (d)	7.110 (t)
H[5]	7.226 (d)	7.584 (d)	7.434 (d)	7.666 (t)	7.402 (d)	7.492 (d)	7.414 (t)	7.315 (d)	7 .336 (m)	7.305 (t)	7.402 (t)	7.158 (d)
H[6]	7.439 (d)	7.601 (d)	7.699 (t)	7.698 (d)	7.411 (d)	7.555 (d)	7.457 (d)	7.463 (t)	7.539 (t)	7.412 (m)	7.427 (d)	7.223 (t)
H[8]	7.658 (d)	7.620 (d)	7.833 (d)	7.772 (d)	7.443 (d)	7.584 (d)	7.521 (d)	7.514 (t)	7.570 (t)	7.587 (t)	7.681 (d)	7.308 (t)
H[11]	7.852 (d)	7.625 (t)	7.851 (d)	7.991 (d)	7.662 (d)	7.609 (d)	7.658 (d)	7.935 (d)	7.658 (t)	7.628 (t)	7.696 (d)	7. 372 (m)
H[12]	8.680 (d)	8.056 (d)	8.135 (t)	8.152 (d)	8.961 (d)	8.752 (d)	8.318 (d)	8.636 (d)	8.607 (d)	8.287 (t)	8.426 (d)	8.408 (d)
H[13]	10.456	9.031	10.358	9.895	9.021	-	10.268	10.028	9.432	9.440	9.696	9.852
H[14]	11.856	-	12.345	10.068	12.732	12.760	12.816S	12.710	10.325	10.852	12.789	-

Antimicrobial activity

The synthesized azo compounds were tested against antimicrobial activity . Antimicrobial analysis was followed using standard agar well diffusion method to study the antimicrobial activity of azocompounds .Each bacterial isolate was suspended in Brain Heart Infusion (BHI) broth and diluted to approximately 10^5 colony forming unit (CFU) per mL. They were flood-inoculated onto the surface of BHI agar and then dried. Five-millimeter diameter wells were cut from the agar using a sterile cork-borer and 30 µL (5µg compound in 500 µL DMSO) of the sample solution were poured into the wells. The plates were incubated for 18 h at 37C for bacteria. Antimicrobial activity was evaluated by measuring the diameter of the zone of inhibition in mm against the test microorganisms. DMSO was used as solvent control. Ciprofloxacin was used as reference antibacterial agent. The tests were carried out in triplicates.

Table-5 (Zone of inhibition in mm)

S.No	Name of the organism	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	Antibiotic disc
	CONTROL	-	-	-	-	-	-	-	-	-	-	-	-	-
1.	Escherichia Coli	20	19	15	12	10	5	8	22	18	10	19	20	15

2.	Bacillus Substilis	23	19	20	25	11	24	20	18	16	20	21	20	10
3.	Streptococcus Mutants	30	24	27	32	20	16	10	17	8	20	19	25	20
4.	Staphylococcus Aureus	27	25	28	29	20	23	19	24	16	12	10	13	20
5.	Pseudomonas Aeruginosa	17	19	10	20	27	25	26	24	20	20	19	23	40

(*S-1, S-2,etc - Sample-1,Sample-2,etc)

Conclusion

The azo compounds with various substituents have been synthesized by simple diazotization reaction of various substituted aromatic amines followed by coupling reaction with substituted aldehydic compounds. The synthesized azo compounds have been characterized by UV, IR and NMR spectroscopic methods. Antimicrobial analysis of synthesized dyes was carried out using standard agar-well diffusion method and screened against five microorganisms viz Escherichia coli, Bacillus substilis, Staphylococcus aureus, Pseudomonas aeruginosa and Streptococcus Mutants. Antimicrobial activity was evaluated by measuring the diameter of the zone of inhibition in mm against test microorganism. The azo compounds synthesized showed excellent results for Spectra and antimicrobial activity. Among all these azo compounds , compound-1 and -4 showed excellent antimicrobial activity, when compared to all the compounds.

Acknowledgement

Authors are thankful to the Management, Principal, Dean of the Research, Head of the department of Chemistry & Head of the department of Clinical nutrition and dietetics and our college Instrumentation lab Incharge, SDNB Vaishnav College For Women, Chrompet , Chennai-44

REFERENCES

1. K. Nejeti , Dyes and Pigments, 2007, 75, 653-657.
2. F. Karci, F. Karci., Dyes and pigments, 2008, 76, 147-157.
3. B. K. Patel, N. K. Prajapati and D. G. Patel Pelagia Research Library Der Chemica Sinica, 2013, 4(6):70-72
4. A. T. Peters, H. S. Freeman, Colour chemistry, the design and Synthesis of organic dyes and pigments, Elsevier App. Sci. Publ., Barking, Essex, UK, 1991, p. 193.
5. H. Kocaokutgen, M. Gur, M. S. Soylu, P. Lonnecke, Dyes Pigm., 2005, 67, 99.
6. P. Gregory, High-technology applications of organic colorants, Plenum Press, New York, 1991, p. 1.
7. Abdalla M. Khedr, Fawaz A. Saad1 Turkish Journal of Chemistry Turk J Chem (2015) 39: 267 – 280
8. S. C. Catino, R. E. Farris, in: Concise Encyclopedia of Chemical Technology, M.Grayson, Ed., John Wiley & Sons, New York, 1985, p.142.
9. H. Ollgaard, L. Frost, J. Galster, O. C. Hansen, Survey of azo Colorants In Denmark: consumption, use, health and Environmental aspects, Ministry of Environment and Energy,Denmark and the Danish Environmental Protection Agency, No. XX, 1998, p. 147.
10. D. Das, A.K. Das, C. Sinha, Anal. Lett.32 (1999) 567.
11. D. Das, A. K. Das, C. Sinha, Talanta 48 (1999) 1013.
12. P.K. Santra, D. Das, T. K. Misra, R. Roy, C. Sinha, S.M. Peng Polyhedron18 (1999) 1909.
13. P. K. Santra, T. K. Misra, D. Das, C. Sinha, A. M. Z. Slawin, J. D. Woollins Polyhedron18 (1999) 2869.
14. M. Camalli, F. Caruso, G. Mattogno, E. Rivarola Inorg. Chim. 6.Acta170(1990)225.
15. M.M. Omar, Ann. Chim. 92 (2002) 601.
16. S. Wu, W. Qian, Z. Xia, Y.Zou, S. Wang, S. Shen, H. Xu, Chem. Phys. Lett.7(2000) 530.
17. B.K. Ghosh, A. Chakravorty, Coord. Chem. Rev95 (1989) 239.
18. S. Wu, W. Qian, Z. Xia,Y. Zou, S. Wang, S. Shen, Chemical physics Letter 330 (2000) 535.
19. W. Nowik, Encyclopedia of separation sciences, Academic Press,. London, 2000, p. 2602. 43. H. Zollinger, Color Chemistry 20.J. Koh , A.J. Greaves., Dyes Pigments, 2001, 50,117. 21. N. Sekar, Colourage., 1999,46,63
22. Bakhsh and Rufchahi, Synthesis, characterization and spectroscopic properties of some new azo dyes derived from 6-aminopyrimidine-2, 4(1H, 3H) – dione, Orient. J. Chem., 2009, 25, 41-45.
23. Naik A. P., Desai K. R. and Patel H. S., Synthesis of azo dyes based on alpha-Naphtholformaldehyde oligomer and their application on textile, Iran. Poly. J., 2001, 10, 1-7.
24. Himani N.Chopde, etal International Journal of ChemTech Research Vol .2, No.3, pp 1823-1830 (2010)
25. K.N. Gaind & J. M. Khanna., Indian J.Pharm., 1964, 26, 34.
26. K. N. Gaind & S.K.Gulati., Indian J.Pharm., 1966, 28,272.
27. L.S.Goodman & A.Gilman, "The Pharmacological Basis of Therapeutics", 4th Edn., MacMillian, New York.,1970, 1111..
28. K.K.Pandey & R. Kaushal., Indian J. Appl. Chem.,1969, 32, 96.
29. K. K. Chaturvedi & R. K. Kaushal., J. Indian Chem. Soc., 1970, 47, 1135.
30. V. A. Modhavadiya Asian Journal of Biochemical and Pharmaceutical Research Issue 1 (Vol. 1) 2011.
31. H.G. Garg, R.A. Sharma, J.Med. Chem.12(1996)1122
32. Mustafa Odabasoglu etal Elsevier.Science direct, Journal of Molecular Structure 840 (2007) 71-89
33. Chatwal G R, Synthetic drugs, (Himalaya Publishing House), 1996, 331.
34. K.M. Rathod and Thakre, Chem Sci Trans., 2013, 2 (1) ,25-28