

Synthesis of Novel Acidic Mono Azo Dyes and an Investigation of Their Use in the Textile Industry

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1,2-hydroxy phenyl azo,8-amino naphthalene, 3,6-disulfonic acid mono sodium salt (HFANS) and its metal complex with chromium (III) salt (ligand metal ratio 1:1) were synthesized as H-acid derivatives. Having an acidic character these dyes are used for dyeing polyamide and protein fibers. Their properties such as dyeing, wash fastness and color classification were investigated according to international standard methods.

Introduction

Acid dyes have found wide application in dyeing wool, polyamide fibers and blends of both these fibers but they have to meet very high requirements as regards their application and fastness¹. It is well known that o,o¹-dihydroxy azo dyes and their metal complexes are principally chromium and cobalt complexes for obtaining dyeing protein and polyamide fibers with excellent light and wash fastness. These dyes are used in electrophotographic or sensor applications for photoconductors². In addition, they are also preferred in high technology areas such as lasers, electro-optical devices and ink-jet printers³.

The present study focused on mono azo acid dyes, which are H-acid derivatives, and investigated their application in the textile industry. The synthesis of HFANS obtained by diazotization of o-hydroxy phenol and coupling with H-acid is described. The metal complexing of HFANS with chromium (III) chloride was carried out in aqueous medium. H-acid (1-amino 8-naphthol-3,6-disulfonic acid) is one of the most important dye intermediates. It is widely used in the chemical industries for the synthesis of direct, acid, reactive and azoic dye, as well as in the pharmaceutical industry^{4,5}.

Materials

UV-visible Spectrophotometer: Ati, Unicam, UV2

Elemental Analysis: Elemental Analyzer mod 1106

Magnetic Susceptibility: Sherwood Scientific Cambridge

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Mass Spectrometer: (Tübitak) Micro mass UK 2LC-Mass

H-NMR: Jeol FX 60Q 60 MHz

Atomic Absorption Spectrophotometer: Ati Unicam 929

Methods

Synthesis

(1,2)- hydroxo phenyl azo,8-amino naphthalene-3,6-disulfonic acid, mono sodium salt (HFANS)

A finely ground powder of the 0.04 mol (4.56 g) o-amino phenol was cooled to -5°C - 0°C and diazotized with 1.4 g, 20% of NaNO_2 at 0°C in hydrochloric acid⁶. Then 0.04 mol (14.6 g) H-acid solution, which was dissolved in water with sodium carbonate, was coupled with the obtained diazonium salt at pH values between 9 and 10. The mixture was stirred for a further 1 h at 0°C . The crude product was separated by acidification and washed with ethyl alcohol twice. The purity of the dye was determined by thin layer chromatography (TLC). The yield of the reaction was 96.7% and its color was reddish violet. It is soluble in water and DMSO. M.P. $> 350^{\circ}\text{C}$. The molecular structure of the compound was explained by analytical and spectroscopic methods such as elemental analysis, UV-visible, FTIR, H-NMR, and MS. Suggested structures of the HFANS are given in Figure 1 and Table 1.

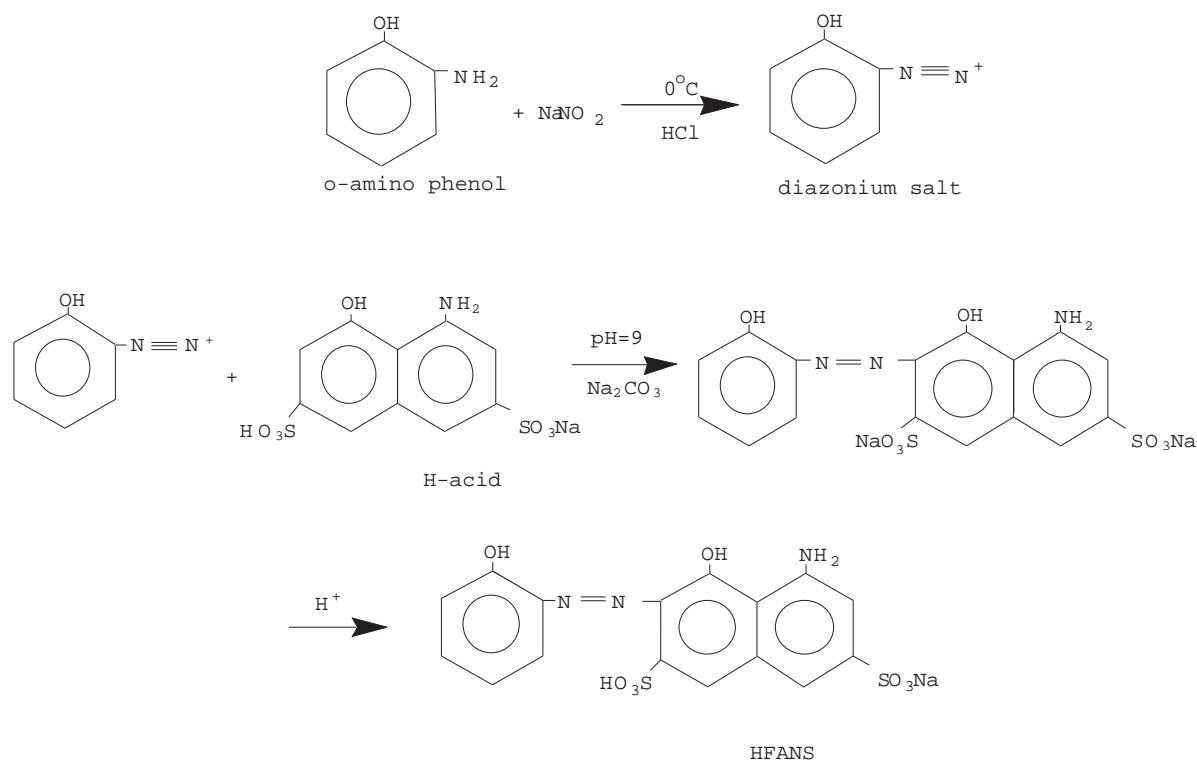


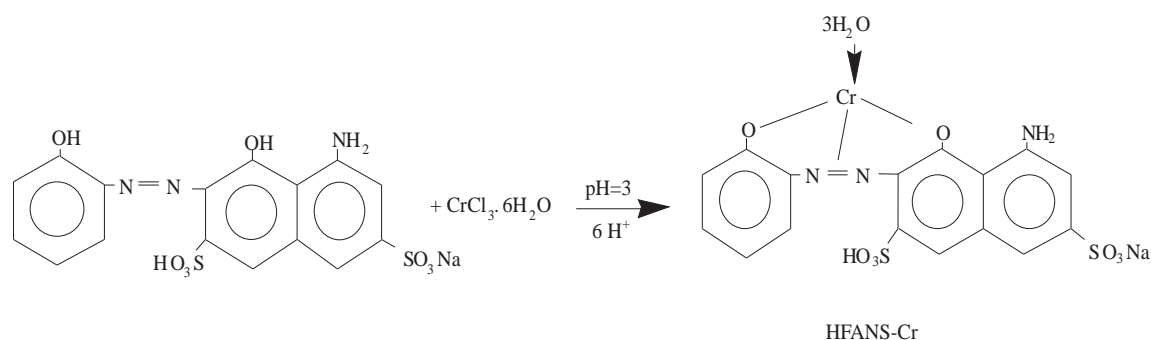
Figure 1. Synthesis of HFANS

Table 1. Some physical properties of the ligand and its metal complex

Dyes	Formula	Color	M.P. (°C)	Elemental Analysis		Yield %
				(C,H,N) ^{calculated}	(C,H,N) ^{found}	
HFANS	C ₁₆ H ₁₂ N ₃ O ₈ S ₂ Na,3H ₂ O	Reddish violet	> 350	(37.35,3.50,8.17)	(37.91,2.99,7.98)	96.7
HFANS-Cr	C ₁₆ H ₁₆ N ₃ O ₁₁ S ₂ Na,Cr,4H ₂ O	Navy blue	> 350	(30.14,2.83,6.60)	(30.22,3.15,7.00)	73.7

Chromium complex of HFANS (HFANS-Cr)

For this procedure 0.21 mmol (0.12 g) HFANS was dissolved in water and 0.21 mmol (0.073 g) Cr(III) chloride solution was added to this solution. The mixture was heated and stirred under reflux at pH 3 for 6 h. The completed reaction mixture was precipitated at pH 6 and filtered hot and washed in ethyl alcohol twice. The purity of the dye was determined by TLC. The yield of the reaction was 73.7% and its color was navy blue. It is soluble in water and DMSO. M.P. > 350°C. Cr(III) (atomic absorption spec.) calculated 8.22% , found 8.04%. The molecular structure of the compound was explained by analytical and spectroscopic methods such as elemental analysis, UV-visible, FTIR, and MS. The molecular structure of this metal complex dye is shown in Figure 2 and Table 1.


Figure 2. Synthesis of HFANS-Cr

Dyeing

All the procedures for dyeing were taken from the literature⁷. The results are listed in Table 2.

Table 2. Some dyeing properties on textile fibers of obtained dyes

Synthesized dyes	Wash fastness		Color classification	
	Protein	Polyamide	Protein	Polyamide
HFANS	2S	4S	19-2816TC	18-3025TC
HFANS-Cr	3S	4S	18-3415TC	15-2205TC

Application of HFANS on protein fiber

Material was added to a solution that included 2-4% H₂SO₄ and 10-20% Glauber salt at 40°C. After 20 min, dissolved dye solution was added to this mixture. After 40 min, temperature was raised to boiling point. The operation was continued for 60 min, followed by washing, and drying with air.

Application of HFANS on polyamide fiber

Material was added to a solution that included 3-4% formic acid and boiled. After 1 h ammonium acetate was added to the solution due to the dark color of the dye, followed by washing, and drying with air.

Application of HFANS-Cr on protein fiber

Material was added to a solution that included 8% H₂SO₄ and 1% Glauber salt at 60°C. After 10 min, dissolved dye solution was added to this mixture. The operation was continued for 3 h. Then it was first washed with water and second, with NH₃-CH₃COONa solution and dried with air.

Application of HFANS-Cr on polyamide fiber

The dye solution was poured into a reaction vessel at pH 7. Material was added to this beaker and the temperature was raised to boiling point over 30 min. Then 1-3% ammonium acetate was added, followed by drying.

Procedure for wash fastness

The reduction cleared, dyed fabrics were tested according to the ISO CO6/C2, 60°C wash test using a suitable detergent. The change in shade and staining of fiber were assessed using a gray scale.

Results and Discussion

UV-visible spectra (water, pH 7)

Absorption bands belonging to the aromatic structure of HFANS were observed at 200-235 nm. In addition, the B band of naphthalene appeared at 315 nm. As expected, there was a band belonging to the azo group at 551 nm. The dye had a high molar absorption coefficient, $\epsilon = 28356$.

The absorption band of HFANS-Cr was observed at 200 nm. The B band of naphthalene appeared at 323 nm. There was a band belonging to the azo group at 619 nm. The dye had a high molar absorption coefficient, $\epsilon = 29527$.

FTIR (KBr, disc, ν cm⁻¹)

IR spectra of the HFANS

The hydroxyl stretching vibration bands were observed to overlap in the 3425-3450 cm⁻¹ region with aromatic NH bands. At 1579 cm⁻¹ the absorption band was assigned to the -N=N- group. The 1506 cm⁻¹ absorption is typical of a naphthalene ring.

IR spectra of the HFANS-Cr

The intense bands at 1556 cm⁻¹ and 1468 cm⁻¹ were due to stretching of the -N=N- and naphthalene group. The other significant broad band in the region 3425 cm⁻¹ is typical of the aromatic -NH and water overlapped bands. The 756 cm⁻¹ is Cr-O stretching band⁸.

¹ H-NMR (DMSO-d₆, δ , ppm)

In the H-NMR spectral data of HFANS were observed Ar-H at 7-8.1 ppm as multiples, and the aromatic NH peak appeared at 3.5 ppm.

We were unable to obtain H-NMR spectra of the HFANS-Cr due to the paramagnetic properties of the metal complex determined by magnetic susceptibility.

MS (MS-Scan EI (Da/e))

Fragments of the molecular structure of HFANS were observed as follows. The tallest peak at 44 amu (atomic mass unit) corresponds to the $C_2H_6N^+$ ion (M-44). The other peaks are fragment ions derived from the parent ion. M-281 ($C_{16}H_{15}N_3O_2^+$), M-127 ($C_{10}H_7^+$), M-159 ($C_{10}H_9ON^+$), M-105 ($C_6H_5N_2^+$).

Fragments of the molecular structure of HFANS-Cr were observed as follows. The highest peak (at 44 amu) corresponds to the positively charged $C_2H_6N^+$ ion (M-44). The other peaks represent cations produced by the breakdown of the HFANS-Cr. M-281 ($C_{16}H_{15}N_3O_2^+$), M-127 ($C_{10}H_7^+$), M-159 ($C_{10}H_9ON^+$), M-105 ($C_6H_5N_2^+$), and at the 52 amu assigned for Cr (M-52).

Conclusion

The color of a dye is deep and dull when the number of azo groups increases in the molecular structure of the dye⁷. Therefore, mono azo dyes are preferred to bis and tris azo dyes (Figure 3). In addition, the washing fastness of mono azo dyes is better than that of others, as shown in Table 3.

Table 3. Comparison of some properties of similar dyes with synthesized dyes

Dyes	Chemical class	Hue	Dyeing	Washing fastness (ISO,S)	Solubility
HFANS	Mono azo	Reddish violed	wool nylon	2 4	Water Ethanol*
HFANS-Cr	Mono azo	Navy blue	wool nylon	3 4	Water Ethanol*
Acid Red 33	Mono azo	Bright red	wool nylon	2 3	Water
Mordant Dye	Mono azo	Dull bluish green	wool silk	5	Water Ethanol*
Mordant Blue 18	Mono azo	Reddish navy	wool	5	Water
Mordant Green 52	Mono azo	Dull bluish green	wool, cotton	4	-
Acid Dye	Bis azo	Deep violet	wool	-	-
Direct Blue 19	Bis azo	Reddish navy	cellulose wool, silk	2	Water
Direct Dye	Bis azo navy	Reddish	cellulose wool, silk	-	Water

*: slightly soluble

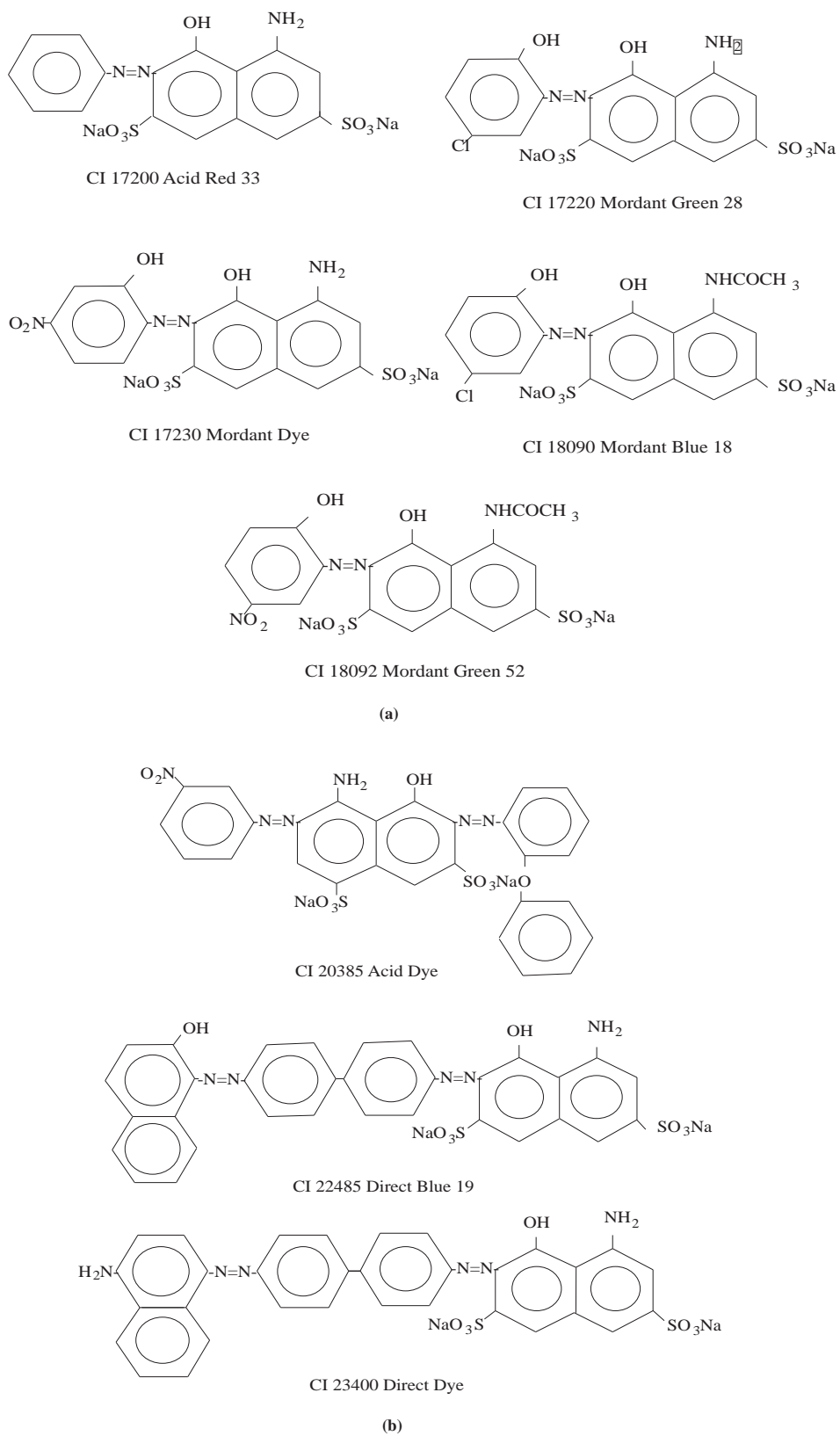


Figure 3. Molecular structures of some azo dyes: (a) mono azo dyes (b) bis azo dyes

HFANS and HFANS-Cr were synthesized as described above and their molecular structures were determined. They were classified according to the International Pantone Textile Color Catalog⁹. The color of HFANS for protein fiber is 19-2816TC and for polyamide fiber is 18-3025TC. The wash fastness of HFANS is 2 S (staining) for protein fiber and therefore it is not good quality. However, we can suggest that HFANS can be used as precursor dye, which is applied to the determination of synthetic fibers, because it is soluble in water. The wash fastness of HFANS for polyamide fiber is 4S and it can be used for dyeing in the textile industry.

The color of HFANS-Cr for protein and polyamide fiber is 18-3415TC and 15-2205TC respectively. The wash fastness of HFANS-Cr for protein fiber is 3S and for polyamide fiber is 4S, and so it can be used for dyeing. In this case, it was observed that the metal complex dye is preferable to the dye without metal.

Acknowledgments

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References

1. K. Bluss, **Dyes and Pigments**, 41, 149-157 (1995).
2. B.R. Hsieh, **Dyes and Pigments**, 14, 287 (1990).
3. A.T. Peters and H.S. Freeman, Color Chemistry, **Elsevier Science**, London, p.286 (1991).
4. G. Hallas and J.H. Choi, **Dyes and Pigments**, 40, 119-129 (1999).
5. S. Wang, S. Shen and H. Xu, **Dyes and Pigments**, 44, 195-198 (2000).
6. Kirk-Othmer Encyclopedia of Chemical Technology, Second completely revised edition (1965- 1970).
7. Y. Özcan., Tekstil Elyaf ve Boyama Tekniği, **İstanbul Üniversitesi Yayınları**, İstanbul, p.597 (1984).
8. F.B., Freeman, D.S. Lee and L.R. Adele., Infrared Spectra and Characteristic Frequencies, **Interscience**, New York, p.731 (1968).
9. PANTONE Textile Color Selector Cotton Edition, Pantone Inc. (1999).
10. Color Index, **The Society of Dyers and Colorist**, Third Edition, 4, USA (1971).