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Synthesis and Application of Monoazo Acid Dyes Containing Trifluoromethyl Group and Their Methyl Analogous on Polyamides

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A new series of monoazo acid dyes containing *m*-trifluoromethyl aniline reacted with various couplers such as Schaeffer acid, N.W. acid, γ-acid and N-(4-sulphophenyl)-3-methyl-5-pyrazolone compound were prepared. These dyes were compared with parallel series of dyes obtained from *m*-toluidine in place of *m*-trifluoromethyl aniline. Subsequently the polyamide fabrics mainly silk, wool and nylon were dyed and their properties such as water repellency, colour depth and fastness properties were determined. Trifluoromethyl based dyes were found to impart improved water repellent properties without impairing any other conventional performance properties, significantly.

Key Words: Monoazo acid dyes, Water repellency, Wettability, Colour depth.

INTRODUCTION

The fundamental finishes in textiles are becoming increasingly popular as the consumer demands are becoming more and more specific. The specific application of textile product will decide the kind of finishes, the fabric is supposed to be undergoing such as wrinkle resistance, water repellency, flame retardance, antimicrobial properties, *etc.* in case of apparel textiles the resistance to wrinkle, dimensional stability and fastness properties to washing and light of the colourants used on them become common requirement. Many times apparel textiles are subjected to relatively more number of washings and thus the finishes which are applied in the post colouration stages gradually show lowering in performance properties as the number of washes increases. Hence the method which can enable one to modify the dyes having the properties of the final speciality finish could be of great promise. Alternatively simultaneous

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dyeing and finishing in one bath could obviously reduce both the costs of production and waste[1]. There are various classes of chemicals introduced for finishing of textiles, which impart water and oil repellency to the fabrics. Fluorochemicals, mainly perfluorinated ones occupy important position in this context[2].

Water repellent finishes are given to a fabric to impart it resistance to stains which are water based. These finishes generally form a water repellent layer on the surface of the material without filling up the interstices, thereby keeping the fabric sufficiently porous to allow water vapour to circulate[3]. Fluorine is the most strongly electronegative element in nature and in fluorine atom the electrons are held close to the atomic nucleus. It is known that the size of fluorine resembles with the size of the hydrogen and the interaction of fluorine atoms with carbon atoms to form strong carbon-fluorine bonds leads to the carbon atoms in fluorocarbons being closely surrounded by fluorine atoms[2]. This is the basis for the low reactivity of fluorochemical finishes and the high degree of protection provided by fluorine atoms to the shielded carbon atom. Also the fluorine exercises an electron withdrawing influence. This property has been used in synthesizing dyes containing fluorine atoms which have water repellency[3,4].

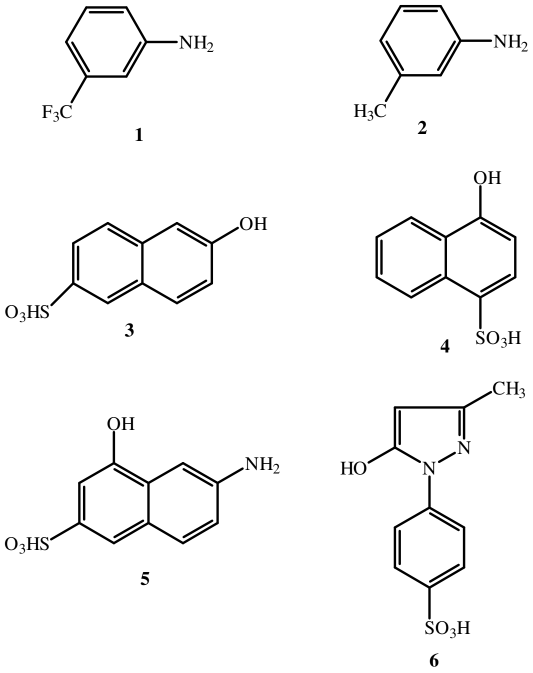
In the present investigation, an attempt is made to synthesize the novel azo acid dyes containing trifluoromethyl group which are used for dyeing of silk, wool and nylon fabric. Diazotized *m*-trifluoromethyl aniline is reacted with the various couplers and the different azo acid dyes were formed. These novel dyes are compared for water repellency and other performance properties with parallel series of dyes obtained from the bases containing *m*-toluidine. The noval azo acid dyes based on trifluoromethyl group are subjected for examining their contribution to water repellency when applied on polyamide fabric. The performance properties of the dyes are also estimated.

EXPERIMENTAL

3-Trifluoromethylaniline (**1**) is of commercial grade obtained from Merck, India. *m*-Toluidine (**2**) is of commercial grade obtained from SD Fine Chemicals, India. Schaeffer acid (**3**), N.W. acid (**4**), γ-acid (**5**), N-(4-sulphophenyl)-3-methyl-5-pyrozolone (**6**) were of commercial grade obtained from Atul (India) Ltd.

Synthesis of Dye 7A: The coupler solution was prepared by dissolving Schaffer acid (**3**) (11.42 g, 0.05 mol) in 100 mL water at a pH 7-8 maintained using sodium carbonate and cooled below 10ºC.

m-Toluidine (5.35 g, 0.05 mol) was added to 50 mL water containing 15.2 mL of 30 % concentrated HCl (0.125 mL) in a beaker surrounded by ice cubes and the reaction mixture was stirred. When the temperature of the reaction mixture was below 10ºC, 20 % $NaNO_2$ (3.50 g, 0.05 mol) was added. The reaction mixture was stirred for about 20 min after complete addition of $NaNO_2$. The reaction mixture was tested to give blue colouration with Congo red paper and weak blue colouration with starch iodide paper indicating a slight excess of nitrous acid.



Structures of the raw materials used for synthesis of dyes

The diazonium salt solution prepared as mentioned above was added to the coupler solution in small amount continuously maintaining the pH between 7 and 8. The temperature of the reaction mixture was kept below 10ºC. After complete addition, the reaction mixture was tested for completion of reaction with H-acid. The mixture was heated to 75-80ºC and excess of 20 % w/v of sodium chloride was added with stirring for salting out of the dye. The separated dye was filtered at 50ºC and dried at 60ºC.

A small amount of the sodium salt of the dye was carefully neutralized using dilute hydrochloric acid at 0-5ºC. The free sulphonic acid thus obtained was filtered, dried at 60ºC and elemental analysis was carried out.

Synthesis of dyes 7B, 7C, 7D, 8A, 8B, 8C and 8D: These dyes were prepared in a similar manner as that of 7A by taking the appropriate amine and coupler. The scheme of synthesis, yield and elemental analysis data are presented in Table-1.

TABLE-1
SCHEMES OF DYE SYNTHESIS, YIELD (%) AND ELEMENTAL ANALYSIS DATA

Dye no.	Scheme of synthesis	Yield (%) / Colour	m.f.	Elemental analysis (%) Found (Calcd.)
7A	2 → 3	65, Reddish orange solid	$C_{17}H_{14}N_2O_4S$	C 59.64 (59.65), H 4.8 (4.09), N 8.21(8.20), S 9.27 (9.27)
7B	2 → 4	60, Orange solid	$C_{17}H_{14}N_2O_4S$	C 59.63 (59.65), H 4.8 (4.09), N 8.21(8.20), S 9.27 (9.27)
7C	2 → 5	62, Reddish pink	$C_{17}H_{15}N_3O_4S$	C 57.13 (57.14), H 4.19 (4.20), N 11.75(11.76), S 8.97 (8.96)
7D	2 → 6	69, Yellow solid	$C_{17}H_{16}N_4O_4S$	C 52.03 (52.4), H 4.07 (4.8), N 14.28(14.29), S 8.15 (8.14)
8A	1 → 3	67, Yellowish orange solid	$C_{17}H_{11}N_2O_4SF_3$	C 53.62 (53.64), F 15.01 (15.00), H 02.63 (2.63), N 7.36 (7.37), S 8.75 (8.73)
8B	1 → 4	66, Orange solid	$C_{17}H_{11}N_2O_4SF_3$	C 53.63 (53.64), F 15.01 (15.00), H 2.62 (2.63), N 7.36 (7.37), S 8.75 (8.73)
8C	1 → 5	60, Brighter reddish pink	$C_{17}H_{12}N_3O_4SF_3$	C 49.63 (49.64), F 13.86 (13.87), H 2.91 (2.92), N 10.21 (10.22), S 7.80 (7.79)
8D	1 → 6	72, Yellow solid	$C_{17}H_{13}N_4O_4SF_3$	C 45.73 (45.74), F 12.73 (12.74), H 2.91 (2.92), N 16.39 (16.37), S 9.69 (9.67)

Characterization of dyes: The elemental analyses of all the dyes were in agreement with their molecular formula as shown in Table-1.

The structure of all these dyes were confirmed by IR spectra recorded in KBr pellets, which showed the expected peaks as shown in Table-2. The pmr spectra recoded in DMSO-d_6 were consistent with the structures. The data are presented in Table-2.

Dyeing of silk, wool and nylon fabrics with synthesized acid dyes: The syntheised monoacid dyes were applied on polyamide fabrics namely silk, wool and nylon-6,6 using standard dyeing methods[5-8].

Colour depth: Dyed samples were evaluated for the depth of the colour by determining K/S values using a Spectra flash ® SF 300, Computer Colour Matching System supplied by Datacolour International, USA.

TABLE-2
INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA DATA OF DYES SYNTHESIZED

Dye No	IR Spectra (KBr pellets)	PMR Spectra (DMSO-d_6)
7A	OH-3458, -N=N-1917, SO_3-1280	δ 2.4 (3H, singlet, CH_3 protons) δ 7.4 (1H, singlet, aromatic protons) δ 7.4-8.1 (8H,multiplet, aromatic protons) δ 11.0 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -NH or -OH protons)
7B	OH-3437, -N=N-1601, SO_3-1181.	δ 2.4 (3H, singlet, CH_3 protons) δ 7.4 (1H, singlet, aromatic protons) δ 7.4-8.2 (7H,multiplet, aromatic protons) δ 9.2 (1H,singlet, aromatic protons) δ 11.2 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -NH or -OH protons)
7C	OH-3391, -N=N-1618, SO_3-1287	δ 2.4 (3H, singlet, CH_3 protons) δ 5.5 (2H, doublet, D_2O exchangeable, -NH_2 protons) δ 7.4-8.8 (8H,multiplet, aromatic protons) δ 11.5 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -OH protons)
7D	OH-3433 -N=N-1959, SO_3-1150	δ 2.4 (3H, singlet, CH_3 protons) δ 3.4 (1H, singlet, -N=C-CH_3 protons) δ 7.4-8.5 (8H,multiplet, aromatic protons) δ 11.2 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -NH or -OH protons)
8A	OH-3468, -N=N-1618, SO_3-1185, CF_3-1328	δ 7.4-8.1 (8H,multiplet, aromatic protons) δ 9.2 (1H, singlet, aromatic protons) δ 11.1 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -NH or -OH protons)
8B	OH-3436, -N=N-1692, SO_3-1189, CF_3 -1289	δ 7.4-8.8 (8H,multiplet, aromatic protons) δ 9.2 (1H, singlet, aromatic protons) δ 11.5 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.2 (1H, singlet, D_2O exchangeable, -NH or -OH protons)
8C	OH-3478, -N=N-1666, SO_3-1157, CF_3-1342.	δ 5.5 (2H,doublet, D_2O exchangeable, -NH_2 protons) δ 7.4-8.8 (7H,multiplet, aromatic protons) δ 9.2 (1H, singlet, aromatic protons) δ 11.5 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -NH or -OH protons)
8D	OH -3430, -N=N-1656, SO_3- 1208, CF_3-1340	δ 3.4 (3H,singlet, -N=C-CH_3 protons) δ 7.4-8.4 (7H,multiplet, aromatic protons) δ 9.3 (1H, singlet, aromatic protons) δ 11.5 (1H, singlet, D_2O exchangeable, -SO_3H protons) δ 15.5 (1H, singlet, D_2O exchangeable, -NH or -OH protons

An average of four readings taken at four different sample areas, was used to obtain the reflectance values and Kubelka Munk K/S function, which was obtained, by using following formula;

$$\frac{K}{S}=\frac{(1-R)^2}{2R}$$

where, R = the reflectance at complete opacity, K = absorption coefficient, S = scattering coefficient.

Assessment of light and wash fastness: Light fastness and wash fastness tests were carried out using standard methods and assessed according to international blue scale (1-8) and grey scale (1-5) respectively[9,10].

Assessment of water repellency

Wettability test for silk fabric: Wettability of the fabric was determined by using the method AATCC Test 39-1980, where, a single drop of water was placed on the surface and time of its absorption by the cloth was measured[11].

Wicking height test for silk fabric: 8" × 1" fabric strip was pinned over a stand supported at convenient height over a petri dish containing water so that the end was just above the surface. A ruler was clamped parallel with the vertical edge of the strip. The strip was lowered, so that one end just touched the water and the stopwatch was just started. The height to which the water rises in 1, 3 and 5 min was noted[12].

Spray test (AATCC 32-1996) for wool and nylon fabric: The spray test measures a resistance of treated fabric to wetting with water. The spray test is carried out for wool and nylon fabrics as per the method described elsewhere[13].

RESULTS AND DISCUSSION

4 Monoazo acid dyes namely **7A, 7B, 7C** and **7D** were synthesized using *m*-toluidine as an amine with four different coupling agents such as Schaeffer acid (**3**), N.W. acid (**4**), γ-acid (**5**) and pyrozolone (**6**) compounds. Subsequently another set of four dyes namely **8A, 8B, 8C** and **8D** containing trifluoromethyl group were synthesized using the same coupling agents as given above. The scheme of synthesis and the characterization data are shown in Table-2.

Colouration properties of the dyes on silk, wool and nylon: Results with respect to colour depth K/S values in terms of deyings obtained for 2 % shades of these dyes on silk, wool and nylon fabric are given in Table-3. The dyeings were evaluated using CIELAB[14,15] system in terms of L*, a*,b*. Results are summarized in Table-4. It is clear from this data that the fluorinated dyes **8A** and **8B** gave lower dye uptake as compared to Dye **7A** and Dye **7B**. However Dye **8C** gave slightly higher value as compared to Dye

TABLE-3
COLOUR DEPTH (K/S) OF DYED SILK FABRIC

Dye no.	Depth of shade (2 %)		
	Silk	Wool	Nylon
7A	11.2461	22.8780	19.4930
8A	8.3090	16.1332	16.1588
7B	16.3185	28.2448	20.3213
8B	3.9910	15.3715	10.0474
7C	6.6553	9.9912	10.3088
8C	8.8381	22.3498	15.0613
7D	7.5415	21.6522	15.0912
8D	9.2016	21.8838	16.6517

TABLE-4
COLOUR COORDINATES OF THE DYES ON SILK, WOOL AND NYLON

Dye no.	Silk			Wool			Nylon		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
7A	65.26	37.78	50.36	49.77	46.11	47.17	58.86	47.32	61.63
8A	70.70	19.34	50.47	58.84	24.52	53.11	62.85	26.83	58.33
7B	59.25	44.22	34.23	43.90	48.32	38.48	49.31	51.69	39.41
8B	53.36	33.68	9.69	57.70	41.27	42.67	63.82	41.53	40.01
7C	56.04	32.65	11.05	39.94	20.99	10.86	42.17	22.13	8.81
8C	74.32	19.85	21.85	39.57	36.60	15.92	42.02	39.88	9.66
7D	80.32	-1.78	59.25	73.36	6.47	81.53	80.50	5.79	85.61
8D	83.94	-5.24	42.38	74.81	2.58	60.85	76.78	6.21	57.81

a Light Source = D65/10° observer.

7C and in Dye **8D**, there was a clear cut and distinct enhancement of K/S value as compared to **7D**. When *m*-trifluoromethyl aniline was coupled with pyrazolone compound, it thus showed enhancement in the K/S values as compared to the dye obtained using *m*-toluidine and pyrazolone. The rest of chemical structure in all the four pairs of dyes remained, respectively same, it is attributed to the substitution by -CF_3 group in place of -CH_3 group, which has varied tinctorial power. In general, the K/S values varied in the following order-wool > nylon > silk. This was valid for all the 4 pairs of the dyes. This could be attributed to greater number of amino groups in wool as compared to silk and nylon. Wool also has greater accessibility to form salt linkage as compared to silk and nylon. Both the kinds of dyes **7A** to **7D** and **8A** to **8D** were able to give good degree of depth of dyeing on silk, wool and nylon. As a result of substitution by trifluoromethyl group, the respective dyes (**8A** to **8D**) showed a varied influence interms of K/S values and also CIELAB colour co-ordinates (Table-4). The influence of fibre structure on the final hue of the shade was also found to depend upon structure of the dye which differed as couplers and diazonium salts varied.

Visible absorption properties of the dyes: The visible absorption properties of all dyes were measured in water and the results are summarized in Table-5. It is seen that, the presence of trifluoromethyl group *meta* to azo group exercised a hypochromic effect of 10 nm as compared to the analogous dyes having methyl group in place of trifluoromethyl group.

TABLE -5
VISIBLE ABSORPTION DATA AND FASTNESS PROPERTIES OF DYES ON SILK, WOOL AND NYLON AT DEPTH OF SHADE, 2 %

Dye no.	Visible spectra		Fabric	Fastness properties	
	Absorption λ_{max} (nm)	log ε		Light fastness	Wash fastness
7A	490	4.24	Silk	5-6	3-4
			Wool	5-6	3-4
			Nylon	4-5	3-4
8A	480	4.20	Silk	4-5	3-4
			Wool	5	3-4
			Nylon	5	3-4
7B	500	4.58	Silk	6-7	3
			Wool	4-5	3
			Nylon	4-5	3
8B	490	4.60	Silk	4-5	3
			Wool	4-5	3
			Nylon	4-5	3
7C	510	4.51	Silk	4-5	3-4
			Wool	3-4	3-4
			Nylon	4	3-4
8C	500	4.55	Silk	4-5	4
			Wool	5	4
			Nylon	4-5	4
7D	410	4.10	Silk	7	3-4
			Wool	6-7	3-4
			Nylon	4-5	3-4
8D	400	4.15	Silk	7	3
			Wool	6	3
			Nylon	5-6	3

Colourfastness properties of the dyes: Performance property such as wash and light fastness of the silk fabric dyed with all the azo acid dyes are summarized in the Table-5. The result indicates that with the trifluoromethyl group substitution, in general there has been no adverse effect on the wash fastness. In almost all the cases, the washing fastness remained in the range of good to very good (3-4), which is quite satisfactory. Similar results were obtained on wool and nylon too.

As far as light fastness properties of dyed silk were concerned, in the case of dye **8A** and dye **8B**, the trifluoromethyl group caused decrease in light fastness by 1 grade, where as in case of dye **8C** and **8D**, there was no change in light fastness. These dyes individually have a differential resistance to light, which varied from grade 4-5 up to 7 which falls well within acceptable limit. When the substrate was changed to wool, there was only ½ grade impairment in case of first two dyes and same was true for nylon too. However, incase of dye **8C** and **8D**, the trifluoromethyl group did cause slight improvement in the light fastness on wool as well as on nylon. Hence in general it could be said that there is no significant deterioration of light fastness as a result substitution by trifluoromethyl group.

Water repellent properties of the dyed fabric

Wettability test: The wettability test of silk fabric dyed with 2 % shade using 8 dyes was carried out as per AATCC 39-1980. The results of wettability are given in Table-6. The results indicate that there was a considerable increase in wettability time of the silk fabric dyed with dyes of **8A** to **8D** series as compared to the silk fabric dyed with dyes **7A** to **7D** series. Among the four dyes containing trifluoromethyl group, dye **8C** showed greater wettability time as compared to all other dyes. The results clearly indicate that the substitution of -CH_3 by -CF_3 in the dye structure distinctly reduced the wettability or increased the water repellency.

TABLE-6
WETTABILITY TEST ON DYED SILK FABRIC AT
DEPTH OF SHADE, 2 %

Dye no.	**7A**	**8A**	**7B**	**8B**	**7C**	**8C**	**7D**	**8D**
Wettability time (s)	10.35	22.99	17.59	27.59	17.99	105.85	15.32	28.18

Control Sample = 10.54 s

Wicking height test: Silk fabric dyed with these dyes was subjected for measurement of wicking height and results are shown in Table-7. It was found that almost in all the case the wicking height of the samples dyed with dyes **8A** to **8D** series was lower than the wicking height of the silk fabric dyed with dyes **7A** to **7D** series, respectively. This further substantiates that substitution of -CH_3 by -CF_3 decreases absorbency characteristics or contributes towards water repellency.

TABLE-7
WICKING HEIGHT TEST FOR DYED SILK FABRIC AT DEPTH OF SHADE 2 %

Dye no	Wicking Height (cm)		
	1 min	3 min	5 min
7A	2.0	3.8	6.5
8A	1.6	2.4	3.6
7B	1.2	2.2	4.5
8B	0.9	1.5	3.4
7C	1.6	3.5	4.6
8C	0.8	1.8	2.7
7D	1.0	2.5	3.2
8D	1.1	3.3	3.9

Spray test: The wool and nylon fabric dyed with dye **7A** to **7D** and **8A** to **8D**, were tested for water repellent properties by AATCC 32-1996 spray test method. From the results, it was found that the spray ratings for the fabric dyed with dyes **8A** to **8D** containing trifluoromethyl group were improved as compared to those dyed with methyl group *i.e.*, **7A-7D** dyes (Table-8). The spray rating obtained in case of wool dyed with **8A** to **8D** was 80 where as it was 70 for wool dyed with dyes **7A** to **7D**. In case of nylon dyed with dyes **8A** to **8D** the rating was improved to 70 and 80 as compared to it being less than 50 for the dyes containing methyl group. This is clearly due to the substitution of hydrogen atom by fluorine in the structure. The trifluoromethyl group containing dyes clearly imparted water repellent properties to wool and nylon.

TABLE -8
SPRAY TEST PERFORMED ON DYED WOOL AND NYLON FABRIC AT DEPTH OF SHADE 2 %

Dye no.	Wool	Nylon
Control Sample	50	< 50
7A	70	< 50
8A	80	70
7B	70	< 50
8B	80	70
7C	70	< 50
8C	80	70
7D	70	< 50
8D	80	80

Conclusion

It was possible to synthesise monoazo acid dyes containing trifluoromethyl groups and these dyes did exhibit not only good yield but also satifactory colouration and performance properties on dyeing with polyamide fabric like silk, wool and nylon. It has been substantiated that such specialty dyes containing trifluoromethyl group in the dye structure can impart the water repellent properties to the fabric on which they are applied. This property is durable as long as the dye is present in the fabric. From the above results dye **8C** and **8D** showed higher water repellency than that of dyes **7C** and **7D** and they also showed over all good performance properties than their methyl analogs.

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