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New 2-aminopyridine containing acid anthraquinone dyes, their application and microbial studies

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New 2-aminopyridine based acid anthraquinone dyes have been synthesized by condensation of bromamine acid with 2-aminopyridine to produce 1-amino-4-(2-amino pyridinyl)anthraquinone-2-sulfonic acid, which is diazotized and coupled with various naphthalene based acid coupling components to get new series of acid anthraquinone dyes. All the synthesized dyes have been characterized by elemental analysis, spectral studies and the dyeing performance on wool, silk and nylon fibres has been assessed. All the dyes give good to very good light fastness on each fibre. The percentage dye-bath exhaustion on different fibres is good and acceptable. The dyed fibres showed moderate to very good fastness to light, washing and rubbing. All the synthesized dyes have been screened for their antimicrobial activity.

Keywords: Anthraquinone, acid dyes, dyeing, wool, silk, nylon

A dye can generally be described as colored, ionizing and aromatic organic compounds, which shows an affinity towards the substrate to which it is being applied in a solution that is aqueous. Dye may also require a mordant to improve the fastness of the dye on the material on which it is applied. In contrast, a pigment generally has no affinity for the substrate and is insoluble. Most of the synthetic dyestuff are synthesized from a few starting materials, such as benzene, naphthalene, phenol, aniline, *etc*. which are obtained from coal-tar. The synthetic dyes are also known as coal-tar dyes.

2-Aminopyridine based acid anthraquinone dyes have found wide application in dyeing wool, polyamide fibres and blends of both fibres[1,2] but they meet very high requirements as regards their application and fastness. The characteristics chromophore of the anthraquinone series consists of one or more carbonyl groups in association with a conjugated system. Anthraquinone dyes and colorants make important contributions to a number of widely different usage groups. The more important are acid, direct, disperse, moderant, vat, solvent and reactive dyes even as pigments[3-8] as a class anthraquinone acid dyes are known for their specific colour and high light fastness characteristics. Anthraquinone acid dyes provide a number of bright fast to light blue and green neither available among the azo dyes nor in fact equaled by any other class. The colour of anthraquinone dyes depends upon substitution among definite lines[9,10].

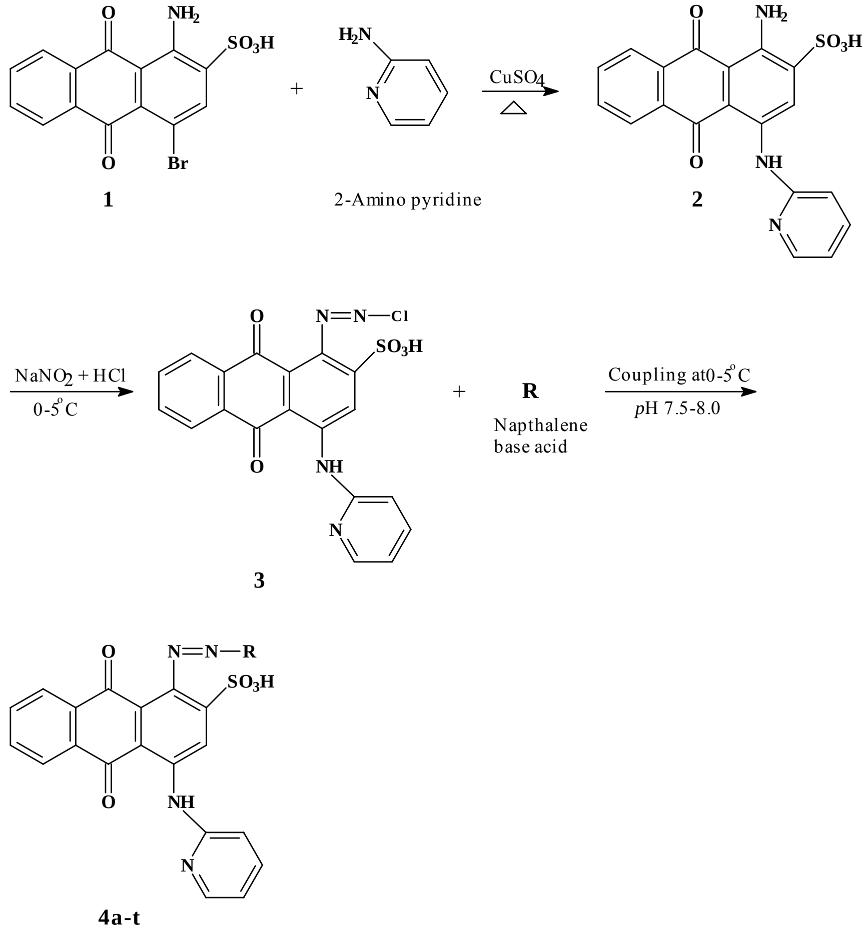
Result and Discussion

This series of dyes have found wide application in dyeing wool, polyamide fibre and blend. In this series chromophoric group such as carbonyl group was condensed with conjugated system like anthraquinone to produce violet colour shades and high light fastness characteristic (**Scheme I**).

The yield of the dyes range from 76% to 86%. The structure were postulated and established based on analytical and spectral evidences. The shades varies from brown to violet depends upon the substituents present and/or the position of the substituents on the ring. The exhaustions range from 65.5% to 81.30% and the fixation range from 78.27% to 92.78%. Most of the dyes have good to excellent rubbing fastness (dry and wet) and this may be attributed to appropriate diffusion of the most of the dyes showed moderate to very good light fastness properties (**Table I**).

Exhaustion and fixation study

The percentage exhaustion of 2% dyeing on wool fabric shows exhaustion 67.00% to 78.00%, on silk fabric shows exhaustion 65.10% to 79.40% and on nylon fabric shows exhaustion 62.00% to 76.62%.



R = Napthalene base acid coupling component

Scheme I

Table I — Dye-bath materials

Materials	for wool	for silk	for nylon
Fibre (g)	2.0 g	2.0 g	2.0 g
Amount of dye (mg)	40.0 mg	40.0 mg	40.0 mg
Glauber salt (20%)	1.5 mL	1.0 mL	1.0 mL
Formic acid soln. (10%)	1.5 mL	1.0 mL	1.5 mL
*p*H	3.0	3.0	3.0
MLR	1.40	1.40	1.40
Dyeing time (min)	60 min	40 min	90 min
Dyeing temp.(°C)	100°C	85°C	100°C
Total volume	80 mL	80 mL	80 mL

The percentage fixation of 2% dyeing on wool fabric shows fixation 78.27% to 91.79%, for silk fabric shows fixation 80.01% to 91.05% and for nylon fabric shows fixation 81.86% to 89.92%. Exhaustion and fixation data of **4a-t** on wool, silk and nylon are given in **Table II**, **III** and **IV**.

Dyeing of fibres

All the dyes **4a-t** were applied on wool, silk and nylon by using different procedure having dye bath material as given below.

Fastness Properties

All the dyes gave fair to very good light fastness on wool, silk and nylon. All the dyes gave good to excellent fastness to washing and rubbing on each fiber. Fastness properties data of **4a-t** are given in **Table V**.

Microbial Studies

All the acid anthraquinone dyes are inactive against both Gram Positive (*Pseudomonas Sp.* and *B.subtilis*) and Gram Negative (*Ceretium* and *E.coli*) bacteria at 100 µg/mL and 200 µg/mL concentration compared to Penicillin, Ampicillin and Amoxicillin.

Table II — Results of exhaustion and fixation study of **4a-t** on wool, silk and nylon

Dye	Wool		Silk		Nylon	
	% Exhaustion	% Fixation	% Exhaustion	% Fixation	% Exhaustion	% Fixation
4a	70.15	89.09	75.18	83.80	67.00	85.82
4b	74.00	87.83	74.25	85.52	68.80	85.75
4c	70.10	86.30	76.80	86.58	63.93	86.04
4d	74.28	85.49	77.83	84.81	66.12	85.44
4e	70.55	88.58	71.85	86.29	62.00	85.48
4f	75.20	90.36	68.22	87.94	68.10	87.37
4g	78.00	89.10	79.40	90.05	69.05	87.62
4h	71.80	91.23	69.82	84.02	76.25	85.90
4i	77.15	84.25	70.25	86.83	68.22	85.74
4$_j$	72.00	87.50	66.45	91.05	70.80	86.86
4k	67.65	89.40	73.95	83.16	74.15	83.61
4l	75.85	86.35	73.20	84.69	70.85	81.86
4m	67.00	91.79	71.80	87.05	76.10	84.76
4n	73.25	86.68	79.30	80.01	76.62	85.48
4o	72.00	88.88	75.85	80.35	74.55	83.16
4p	67.50	87.40	77.85	85.42	71.17	89.92
4q	68.90	88.53	71.85	80.29	72.60	87.47
4r	72.82	91.31	73.98	87.86	75.67	83.25
4s	70.15	89.80	65.10	90.62	69.00	83.33
4t	74.10	78.27	73.93	87.92	64.50	84.49

Table III — Calibration data for exhaustion study of acid dyes

Substrate for dyeing : Wool (2.0 g), Silk (2.0 g) and Nylon (2.0 g)
Medium of spectral study : Aqueous

Dye	Wave length (nm)	Absorbance of dye solution at specified wavelength Conc. × 10^{-3} mg mL^{-1}				Slope of linear plot K*
		4.0	8.0	12.0	16.0	
4b	470	0.060	0.120	0.180	0.240	15.0
4l	489	0.090	0.180	0.271	0.360	22.5
4t	435	0.110	0.220	0.329	0.44	27.5

Absorbance =K*(Conc. × 10^{-3} mg mL^{-1})

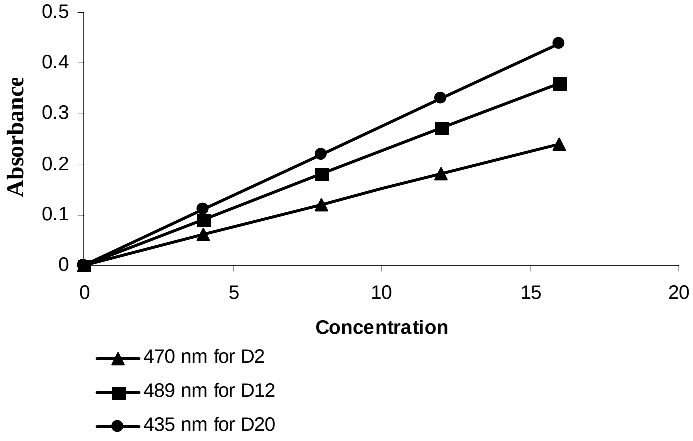
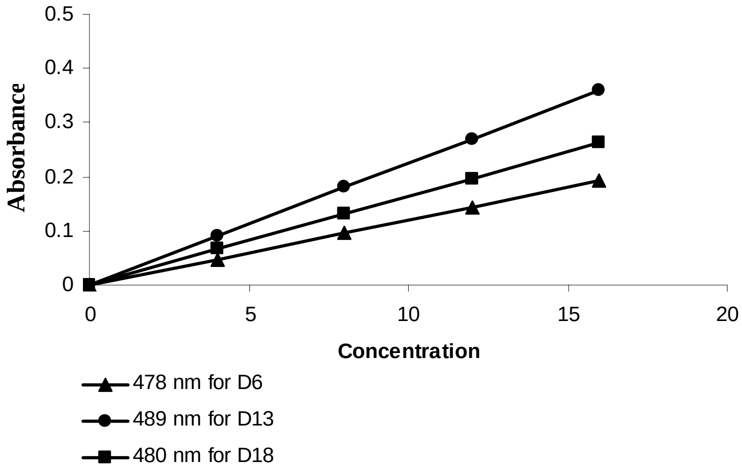


Table IV — Calibration data for fixation study of acid dyes

Substrate for dyeing: Wool (2.0 g), Silk (2.0 g) and Nylon (2.0 g)
Medium of spectral study: Conc. Sulfuric acid

Dye No.	Wave length (nm)	Absorbance of dye solution at specified wavelength Conc. × 10^{-3} mg mL^{-1}				Slope of linear plot K*
		4.0	8.0	12.0	16.0	
4f	478	0.048	0.096	0.143	0.192	12.00
4m	489	0.090	0.180	0.270	0.360	22.5
4p	480	0.066	0.132	0.197	0.264	16.5

Absorbance =K*(Conc. × 10^{-3} mg mL^{-1})



All the acid anthraquinone dyes are inactive against *C.albicans* at 100 μg/mL and 200 μg/mL concentration compared to Amphotericine-B.

Experimental Section

The homogeneity of all the dyes has been checked by TLC[11], IR spectra were recorded in KBr pellets on a Perkin Elmer Model 881 spectrometer and ^{1}H NMR spectra on Bruker Avance II 400 NMR spectrometer (SAIF, Chandigarh, Panjab University) using TMS as internal standard and DMSO-d_6 as solvent. Absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analysis of C, H and N was carried out on Carlo Erba 1108 instruments. The light fastness was assessed in accordance with BS: 1006-1978 (Ref. 12), the rubbing fastness test was carried out with corkmeter (Atlas) in accordance with AATCC-1961 (Ref. 13) and the wash fastness test in accordance with IS: 765-1979 (Ref. 14).

1-Amino-4-(2-pyridinylamino)anthraquinone-2-sulfonicacid, 2

Bromamine acid **1** (0.1 mole) was dissolved in 400 mL hot water (70-80°C), 2-amino pyridine (0.1 mole), acid binding agent sodium bicarbonate (0.2 mole), copper sulfate (0.5g) and ferrous sulfate (0.5 g) catalysts were then added to it. The reaction mixture was stirred and heated to 90°C. Maintained temperature 90°C for 6 hr under stirring. Charcoal (1 g) was added and stirred for 15 min and the solution was filtered by slowly adding diluted hydrochloric acid (1:1) under stirring. The product was salted out by adding sodium chloride, cooled to RT, stirred for 30 min at RT, filtered and washed with 10% w/v brine solution and then dried (85% yield).

IR (KBr): 3515, 3410 (-NH_2), 3310 (-NH-), 1270 (C-N), 1675 (C=O), 1220, 1070 cm^{-1} (-SO_3H); ^{1}H NMR: δ 9.34 (-NH-, 1H, s), 4.95 (-NH_2, 2H, s), 1.90 (-SO_3H, 1H, s), 7.15-8.26 (Ar-H anthraquinone, 5H, m), 6.78-7.95 (Ar-H pyridine, 5H, m).

Diazotization of 1-amino-4-(2-aminopyridinyl)-anthraquinone-2-sulfonic acid, 3

The solution of 1-amino-4-(2-aminopyridinyl)-anthraquinone-2-sulfonic acid, **2** (0.01 mole) was prepared in water. Hydrochloric acid (0.015 mole) was added to this and stirred well, the solution was cooled to 0-5°C in an ice bath. A solution of sodium

Table V — Fastness properties of acid dyes on wool, silk and nylon

Dye	Wool				Silk				Nylon			
	Light	Wash	Rubbing		Light	Wash	Rubbing		Light	Wash	Rubbing	
			Dry	Wet			Dry	Wet			Dry	Wet
4a	4	3	5	4	3-4	3-4	3	3-4	4	3	4	5
4b	4	3-4	4	3	3	3-4	3	3	4	4	4	4
4c	3	2	3-4	3	5-6	3	3	3-4	3-4	4-5	4-5	4
4d	3-4	3-4	3	3-4	3-4	3	3-4	4	4	5	4	3
4e	3	4	4	3	5	4-5	3-4	3	3-4	3-4	3	3-4
4f	3-4	3-4	3	3	4-5	4	3-4	4-5	4	4	3-4	3
4g	3	4	3-4	4	3-4	3-4	4	3	4-5	3	3	3
4h	4	3	3	3-4	4	3	3-4	4	3-4	4	3-4	3-4
4i	3-4	3	4	3-4	4	3	4	4	3	3	3-4	4
4j	4	4	3	3	3-4	3	3-4	3-4	4	4	3	3
4k	5-6	3	3-4	3-4	5	3-4	4	3-4	5	4	3-4	3-4
4l	3	3-4	3-4	5	4-5	4-5	3	4	4	4-5	4	4
4m	4	3	4	3	3	4	3-4	3	4-5	4	3-4	3
4n	4	4	3-4	5	3	3-4	4	3-4	3-4	3-4	3	4
4o	4-5	5	3	2-3	4-5	3-4	3-4	4	4	3	4	3
4p	4	3-4	3-4	3-4	4	3	4	3-4	5	5	4	4
4q	3	3-4	3-4	3	4	3	3-4	3	3-4	4	3	3-4
4r	4	4	4	3-4	5	4	4	3-4	4	3	3-4	3
4s	4	3-4	4	3-4	4-5	4	4	3-4	5-6	4	4	3-4
4t	3	3-4	3-4	3-4	4	3	4	3-4	3	4-5	3	4

Light: Poor-1, Slight-2, Moderate-3, Fair-4, Good-5, Very good-6 and Excellent-7
Wash and Rubbing : Poor-1, Slight-2, Moderate-3, Fair-4, Good-5, Very good-6 and Excellent-7

nitrite ($NaNO_2$, 0.015 mole) in water (8 mL) previously cooled to 0-5°C, was then added over a period of 5 min with stirring. The stirring was continued for 1 hr, maintaining the same temperature with positive test for nitrous acid on starch iodide paper. After stirring for 1 hr, excess of nitrous acid was destroyed with required amount of a solution of sulfamic acid. The resulting diazo solution was obtained at 0-5°C, and was used for subsequent coupling reaction.

Coupling of diazo solution with J-acid, 4

J-acid (2.39 g, 0.01 mole) was suspended in water (20 mL) and dissolved at neutral *p*H in sodium carbonate (10% w/v) to obtain a clear solution. The solution was cooled to below 0-5°C in an ice bath. To this well stirred solution, diazo chloride solution **3** was added dropwise over a period of 10-15 min maintaining the *p*H 7.5-8.0 by simultaneous addition of sodium carbonate solution (10% w/v). The stirring was continued for 3 hr maintaining the temperature between 0-5°C. The reaction temperature was then raised to 60°C and sodium chloride added to precipitate the coloring material. The stirring was continued for 1 hr. The dye was filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90°C and extracted with DMF. The DMF extract was coupled with excess of chloroform. The dye thus obtained was filtered, washed with chloroform and dried at 60°C (81% yield).

The same procedure was adopted for various naphthalene base acid coupling components such as gamma acid, *m*-amino benzoyl k-acid, N-methyl J-acid, sulfogamma acid, chromotropic acid, violet acid, N-phenyl J-acid, G-acid, R-acid, N-benzoyl J-acid, epsilon acid, schaeffer acid, acetyl H-acid, N-(3-sulfophenyl)-gamma acid, acetyl gamma acid, *m*-aminobenzoyl H-acid, acetyl J-acid, H-acid and N-benzoyl H-acid. Characterization data and ^{1}H NMR data of all the dyes are given in **Table VI** and **VII** respectively.

Table VI — Characterization data of **4a-t**

Dye	Coupling component	Mol. Formula	Yield (%)	Found (Calcd) % C	H	N	R_f Value
4a	J-aci4	$C_{29}H_{17}O_9N_5S_2Na_2$	84	50.46 (50.51	2.41 2.47	10.10 10.16)	0.44
4b	Gamma acid	$C_{29}H_{17}O_9N_5S_2Na_2$	76	50.47 (50.51	2.42 2.47	10.11 10.16)	0.43
4c	*m*-Amino benzoyl K-acid	$C_{36}H_{21}O_{13}N_6S_3Na_3$	78	47.41 (47.47	2.22 2.31	9.17 9.23)	0.40
4d	N-methyl J-acid	$C_{30}H_{19}O_9N_5S_2Na_2$	80	51.16 (51.21	2.64 2.70	9.90 9.96)	0.38
4e	Sulfogamma acid	$C_{29}H_{16}O_{12}N_5S_3Na_3$	84	43.93 (43.99	1.97 2.02	8.79 8.85)	0.42
4f	Chromotropic acid	$C_{29}H_{15}O_{13}N_4S_3Na_3$	81	43.90 (43.94	1.83 1.89	7.01 7.07)	0.49
4g	Violet acid	$C_{29}H_{15}O_{12}N_4S_3Na_3$	79	44.79 (44.84	1.89 1.93	7.18 7.22)	0.36
4h	N-phenyl J-acid	$C_{35}H_{21}O_9N_5S_2Na_2$	84	54.83 (54.90	2.69 2.74	9.09 9.15)	0.50
4i	G-acid	$C_{29}H_{15}O_{12}N_4S_3Na_3$	78	44.78 (44.84	1.88 1.93	7.19 7.22)	0.42
4j	R-acid	$C_{29}H_{15}O_{12}N_4S_3Na_3$	80	44.77 (44.84	1.89 1.93	7.18 7.22)	0.45
4k	N-benzoyl J-acid	$C_{36}H_{21}O_{10}N_5S_2Na_2$	77	54.42 (54.47	2.60 2.65	8.78 8.83)	0.37
4l	Epsilon acid	$C_{29}H_{15}O_{12}N_4S_3Na_3$	81	44.78 (44.84	1.89 1.93	7.18 7.22)	0.46
4m	Schaffer’s acid	$C_{29}H_{16}O_9N_4S_2Na_2$	85	51.59 (51.63	2.31 2.37	8.27 8.31)	0.41
4n	Acetyl H-acid	$C_{31}H_{18}O_{13}N_5S_3Na_3$	81	44.61 (44.66	2.09 2.16	8.36 8.40)	0.43
4o	N-(3-sulfophenyl)-Gamma acid	$C_{35}H_{20}O_{12}N_5S_3Na_3$	78	48.39 (48.44	2.23 2.30	8.01 8.07)	0.38
4p	Acetyl gamma acid	$C_{31}H_{19}O_{10}N_5S_2Na_2$	81	50.82 (50.89	2.54 2.60	9.52 9.57)	0.47
4q	*m*-Amino benzoyl H-acid	$C_{36}H_{21}O_{13}N_6S_3Na_3$	85	47.42 (47.47	2.25 2.31	9.18 9.23)	0.40
4r	Acetyl J-acid	$C_{31}H_{19}O_{10}N_5S_2Na_2$	86	50.83 (50.89	2.56 2.60	9.50 9.57)	0.44
4s	H-acid	$C_{29}H_{16}O_{12}N_5S_3Na_3$	78	43.38 (43.44	1.97 2.02	8.79 8.85)	0.39
4t	N-benzoyl H-acid	$C_{36}H_{20}O_{13}N_5S_3Na_3$	80	48.22 (48.27	2.18 2.23	7.77 7.82)	0.43

Table VII — ^{1}H NMR spectral data of **4a-t**

Dye	^{1}H NMR
4a	-NH- (1H, s, 9.23), $-CH_2-$ (2H, t, 2.38), $-NH_2$ (2H, s, 3.80) -OH (1H, s, 5.24), Ar-H (9H, m, 7.20-8.45)
4b	-NH- (1H, s, 9.28), $-CH_2-$ (2H, t, 2.48), $-NH_2$ (2H, s, 3.74) -OH (1H, s, 5.27), Ar-H (9H, m, 7.22-8.39)
4c	-NH- (1H, s, 9.20), $-CH_2-$ (2H, t, 2.50), $-NH_2$ (2H, s, 3.72) -OH (1H, s, 5.14), Ar-H (12H, m, 7.17-8.34), -NHCO- (1H, s, 9.62),
4d	-NH- (1H, s, 9.32), $-CH_2-$ (2H, t, 2.41), -OH (1H, s, 5.16), Ar-H (9H, m, 7.22-8.45)
4e	-NH- (1H, s, 9.30), $-CH_2-$ (2H, t, 2.46), $-NH_2$ (2H, s, 3.77) -OH (1H, s, 5.20), Ar-H (8H, m, 7.18-8.32)

--*Contd*

Table VII — ^{1}H NMR spectral data of **4a-t** — *Contd*

Dye	^{1}H NMR
4f	-NH- (1H, s, 9.23), -CH$_2$- (2H, t, 2.35), -OH (1H, s, 5.18), Ar-H (8H, m, 7.32-8.40)
4g	-NH- (1H, s, 9.34), -CH$_2$- (2H, t, 2.35), -OH (1H, s, 5.18), Ar-H (9H, m, 7.10-8.22)
4h	-NH- (1H, s, 9.24), -CH$_2$- (2H, t, 2.43), -OH (1H, s, 5.16), Ar-H (13H, m, 7.31-8.45)
4i	-NH- (1H, s, 9.26), -CH$_2$- (2H, t, 2.47), -OH (1H, s, 5.08), Ar-H (9H, m, 7.24-8.41)
4j	-NH- (1H, s, 9.23), -CH$_2$- (2H, t, 2.44), -OH (1H, s, 5.16), Ar-H (9H, m, 7.20-8.43)
4k	-NH- (1H, s, 9.29), -CH$_2$- (2H, t, 2.40), -OH (1H, s, 5.22), Ar-H (13H, m, 7.31-8.46), -NHCO- (1H, s, 9.76)
4l	-NH- (1H, s, 9.27), -CH$_2$- (2H, t, 2.42), -OH (1H, s, 5.19), Ar-H (9H, m, 7.25-8.36)
4m	-NH- (1H, s, 9.35), -CH$_2$- (2H, t, 2.47), -OH (1H, s, 5.24), Ar-H (10H, m, 7.27-8.38)
4n	-NH- (1H, s, 9.31), -CH$_2$- (2H, t, 2.50), -OH (1H, s, 5.20), Ar-H (8H, m, 7.24-8.35)
4o	-NH- (1H, s, 9.32), -CH$_2$- (2H, t, 2.43), -OH (1H, s, 5.17), Ar-H (13H, m, 7.12-8.36)
4p	-NH- (1H, s, 9.36), -CH$_2$- (2H, t, 2.53), -OH (1H, s, 5.15), Ar-H (7.15-8.33), -NHCO- (1H, s, 9.75)
4q	-NH- (1H, s, 9.25), -CH$_2$- (2H, t, 2.46), -OH (1H, s, 5.20), Ar-H (12H, m, 7.28-8.46), -NHCO- (1H, s, 9.60)
4r	-NH- (1H, s, 9.28), -CH$_2$- (2H, t, 2.41), -OH (1H, s, 5.19), Ar-H (9H, m, 7.25-8.36), -NHCO- (1H, s, 9.71)
4s	-NH- (1H, s, 9.37), -CH$_2$- (2H, t, 2.48), -NH$_2$ (2H, s, 3.71) -OH (1H, s, 5.12), Ar-H (8H, m, 7.25-8.38), -NHCO- (1H, s, 9.64)
4t	-NH- (1H, s, 9.34), -CH$_2$- (2H, t, 2.54), -OH (1H, s, 5.14), Ar-H (13H, m, 7.26-8.45), -NHCO- (1H, s, 9.67)

Conclusion

The shades of 2-aminopyridine base acid anthraquinone dye varies from brown to violet depending upon the position of the substituents present and/or the position of the substituents on the naphthalene ring. The dyes gave excellent uniformity of coloration on wool, silk and nylon. A remarkable degree of levelness indicates good penetration and affinity of these dyes to the fabric. The newly synthesized 2-aminopyridine containing acid anthraquinone dye coupled with *m*-amino benzoyl k-acid, sulfogamma acid, N-benzoyl J-acid, epsilon acid and N-(3-sulfophenyl)-Gamma acid gave fair to very good light, washing and rubbing fastness on each fabric.

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