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Structure and Dyeing Properties of Some Anthraquinone Violet Acid Dyes

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ABSTRACT

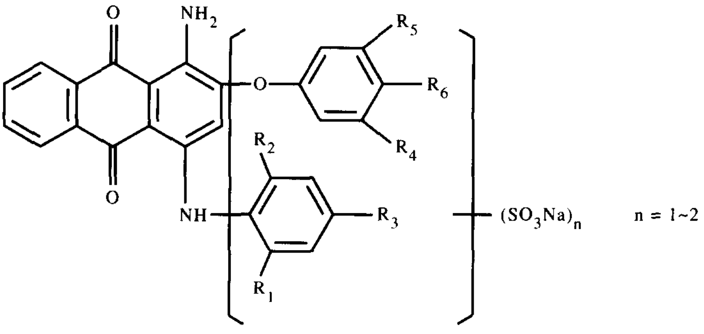
Six violet acid dyes derived from bromaminic acid were prepared and their structures were determined via UV–Vis, IR, ^{1}H-NMR and MS techniques. The colour, fastness and dyeing rate of these dyes were also measured and compared. It was found that the dyes, with one exception, could be used to dye wool, silk and polyamide fibers with excellent fastness to light, wet treatment, rubbing and high dye uptake, having intense brilliant bluish violet hues. *© 1997 Elsevier Science Ltd*

Keywords: anthraquinone violet acid dyes, structure, dyeing properties, tertbutylphenol, iso-octylphenol.

INTRODUCTION

Violet acid dyes with a brilliant hue and excellent fastness were introduced in the 1960–1970 period [1,2]. Although violet acid dyes of the copper complex azo type and of the triphenylmethane type are available, the colour of the former is dull and the fastness to light of the latter very poor. The anthraquinone violet acid dyes can be used for dyeing wool, silk and synthetic polyamide fibers in bright shades of high fastness to light [3].

Violet anthraquinone acid dyes can be synthesized via condensation of 1-amino-4-bromo-2-anthraquinone sulfonic acid (bromaminic acid) with a di- or trialkyl-aniline and subsequent condensation with an alkylphenol followed by sulfonation. Whilst the general formula of such dyes has been outlined, so the number of sulfonic acid groups and their orientation in the phenoxy residue have not been reported [1–7].



Dye No	R_1	R_2	R_3	R_4	R_5	R_6
I	Me	Me	Me	H	H	iso-octyl
II	Me	Me	Me	H	H	tert-Butyl
III	Me	Me	Me	Me	Me	H
IV	Me	H	Me	H	H	tert-Butyl
V	Me	Me	H	H	H	tert-Butyl
VI	Me	Me	H	H	H	iso-octyl

Fig. 1. Structure of synthesised dyes.

In the present paper, six anthraquinone violet acid dyes (Fig. 1) were synthesized. The structures of the dyes were evaluated by UV–Vis, IR, ^{1}H-NMR and MS spectra techniques. The colour and dyeing properties of the dyes were measured and the influence of dye structure on hue and dyeing properties is discussed.

EXPERIMENTAL

Instrumental

Instruments used were a Nicolet 5DX FT-IR Spectrometer (Nicolet Co. American), Carl Zeiss Jena Specord UV–Vis meter (CARL ZEISS JENA Co. G.D.R.), Bruker AM500 NMR Spectrometer (Bruker Co. Swiss), JMS-DX300 MS meter (JEOL Co. Japan), and Colour-Eye (Macbeth Co. Hong Kong).

Chemicals

All Chemicals used were of C.P. and A.R. grade.

1-Amino-4-arylamino-2-anthraquinone sulfonic acids were prepared by using the method previously described [8].

Synthesis of 1-amino-2-(4′-tertbutylphenoxy)-4-arylamino-anthraquinones

A mixture of the appropriate arylamino compound (0.05 mol), 4-tert-butylphenol (0.67 mol) and 50% aq. potassium hydroxide (0.27 mol) was heated and the mixture began to melt at about 120°C. Reaction was continued for 1–1.5 h, with stirring, and with removal of water produced in the reaction. The temperature was then raised to 220–230°C and the mixture then heated for 4 h at 220°C. After cooling to 120°C, 10% aq. sodium hydroxide (500 ml) was added and the mixture stirred for 1 h, cooled to 70–80°C, and then filtered. The residue was washed with warm water until neutral and then dried. Yield, 90%. TLC indicated that the product was a homogeneous violet material (silica gel.; eluant:*n*-butanol:*n*-butyl acetate:acetic acid:water = 3:3:0.5:3).

1-Amino-2-(3′,5′-dimethyl phenoxy-)-4-arylaminoanthraquinones were prepared similarly.

Synthesis of 1-amino-2-(4′-iso-octyl phenoxy-)4-arylamino-anthraquinones

A mixture of the appropriate arylamino compound (0.05 mol), 4-iso-octylphenol (0.35 mol) and 50% aq. potassium hydroxide (0.18 mol) was heated to melting at about 120°C. Reaction was continued for 1–1.5 h with stirring until all water evolved in the reaction was eliminated. The temperature was then raised to 220–230°C and the mixture heated for 4 h at 200–220°C and then cooled to 100°C. Alcohol (200 ml) was added at such a rate to keep the temperature of the mixture unchanged. After stirring the mixture at reflux for 1 h, the required aryloxy substitution product deposited, and after standing, whilst cooling to room temperature, the product was filtered, washed with warm water and dried. TLC, one violet spot (silica gel. eluant:-cyclic hexane:ethyl acetate = 9:1) yield 85–90%.

Sulfonation

The appropriate aryloxy compound (0.05 mol) in 10% oleum (1.90 mol) was sulfonated at 30–40°C for 2 h. The reaction mixture was then stirred for 2 h at 40–50°C and then poured onto ice. The precipitate was filtered. The residue was dissolved in water, the pH adjusted with 20% sodium hydroxide to 6.5–7, and the liquor then salted and filtered, dried to give dye 1 (R_1, R_2, R_3 = Me, R_4, R_5 = H, R_6 = iso-octyl phenoxy) (from 40 g of commercial product, 180% standard dye was obtained.)

Purification of dyes

The dyes were dissolved in water and hydrochloric acid 36–38% was added to adjust the overall HCl concentration to 3–5%; the mixture was then stirred for 1–2 h to ensure that the 2-sodium sulfonate was completely converted into the free acid. The dyes were then filtered and dried. The dyes were finally purified by extraction, TLC and recrystallization from appropriate solvents (e.g. alcohols, DMF).

Dyeing procedures

Wool pieces were immersed in a dyebath containing the dye solution (at 1% depth), 10% sodium sulfate, 1% acetic acid and 0.5% perpgel at 30–40°C with a liquor ratio of 50:1. The dyebath was heated to 90–95°C over 30–40 min, held for 30 min and then heated to boiling over 5 min and then at the boil for 10 min. The bath was cooled to room temperature and the dyeings washed and dried.

The dyeing curves were determined as follows. From 200 ml of the above mentioned dyebath solution, 1 ml was removed and diluted to 25 ml with water. There was then added 1 ml of this solution containing all above additives, except for the dye, to the dyebath, in order ensure the dyebath volume remained constant. A wool piece (4.0 g) was added to dyebath. The dyebath was heated to 30°C over 20 min and the temperature of the dyebath was then raised by 10°C over every 10 min. After each 10 min interval, 1 ml of dye liquor was removed and diluted to 25 ml with water; 1 ml of the appropriate dyebath liquor was added to retain constant volume. The dye uptake was then calculated by measuring the optical densities of the appropriate dye liquors relative to the original dye solution.

The fastness properties of the dyeings were measured in accordance with GB-8427, GB-3920, GB-3921, GB-3922 (China), which are similar to ISO standards.

RESULTS AND DISCUSSION

Characterisation data

Analytical data for the dyes are shown in Table 1 and Figs 2 and 3.

The UV–Vis spectra showed typical absorption of the anthraqunone chromophore in the range 260–270 nm and 560–575, 600–603 nm.

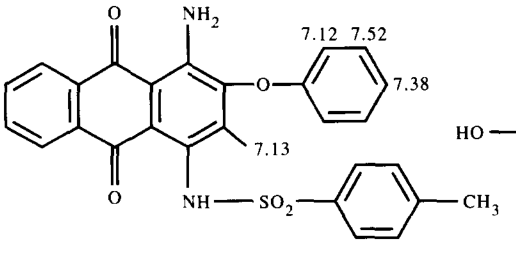
The vibrational band of the carbonyl group in anthraquinone is usually present around 1681 cm^{-1}, but an intramolecular hydrogen bond between the carbonyl group and groups such as NH_2, NH or OH on the 1-position of the anthraqunone nucleus leads to a decrease of the vibrational frequency [9]. The IR spectra of the dyes synthesized show typical bands near 1660 and 1616 cm^{-1}, and only the vibrational frequency was observed at 1632 cm^{-1} for dye **VI**.

In the ^{1}H-NMR spectra, it was noted that the chemical shift of the protons on the 3-position were affected by the methyl groups in the 4-phenylamino

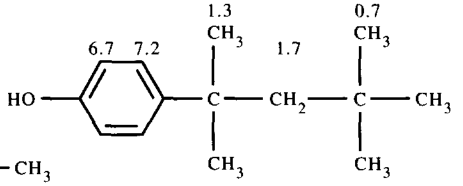
TABLE 1
UV–Vis, IR Data of the Dyes

Dye No.	*IR(K Br) cm^{-1}*	*UV–Vis (water)λ_{max} (nm)*	*ϵ(liter mol^{-1}cm^{-1})*
I	1664.5, 1616.5 (C=O)	560	1.516×10^4
	1180.5, 1022.3 (SO_3H)	603	
	3435.2, 3279.3, 1572.1, 1278.9 ($C\text{-}NH_2$, C-NH-)		
	3049.4, 2859.4 (CH_3), 1230.7 ($C(CH_3)_3$)		
II	1666.6, 1616.5 (C=O)	558	1.462×10^4
	1180.5, 1024.3 (SO_3H)	600	
	3435.2, 3271.1, 1572.1, 1278.9 ($C\text{-}NH_2$, C-NH-)		
	2959.4, 2799.4 (CH_3), 1228.7 ($C(CH_3)_3$)		
III	1660.8, 1616.5 (C=O)	562	1.274×10^4
	1182.4, 1020.4 (SO_3H)	603	
	3435.2, 3279.1, 1570.2, 1277.0 ($C\text{-}NH_2$, C-NH-)		
	2959.4, 2863.4 (CH_3),-(no $C(CH_3)_3$)		
IV	1660.8, 1616.5 (C=O)	575	1.270×10^4
	1190.2, 1028.1 (SO_3H)	603	
	3435.2, 3271.1, 1572.1, 1277.0 ($C\text{-}NH_2$, C-NH-)		
	2959.4, 2831.3 (CH_3), 1232.6 ($C(CH_3)_3$)		
V	1660.8, 1618.4 (C=O)	558	1.221×10^4
	1168.9, 1026.2 (SO_3H)	594	
	3435.2, 3271.1, 1570.1, 1280.8 ($C\text{-}NH_2$, C-NH-)		
	2959.4, 2863.4 (CH_3), 1228.7 ($C(CH_3)_3$)		
VI	1632.0 (C=O)	586	1.340×10^4
	1185.9, 1026.4 (SO_3H)	603	
	3433.2 -, 1585.5, 1279.2 ($C\text{-}NH_2$, C-NH-)		
	2956.4,- (CH_3), 1230.7 ($C(CH_3)_3$)		

residue. In 1-amino-2-phenoxy-4-*p*-methyl benzene sulfonyl aminoanthraquinone (in which there is no methyl group ortho to the 4-benzene sulfonyl amino group), the chemical shift of the proton on the 3-position was in the region of 7.13 ppm for (**VII**) [10]; when both *ortho* positions were substituted by methyl groups, the shifts were displaced to 6.94 and 6.89 ppm for dyes **I** and **II-A**, **II-B**, respectively. The chemical shifts of the protons on the 2-aryloxy residue of dyes **I** and **II-A**, **II-B** were similar to those reported in the literature for (**IIX**) [11].



VII



IIX

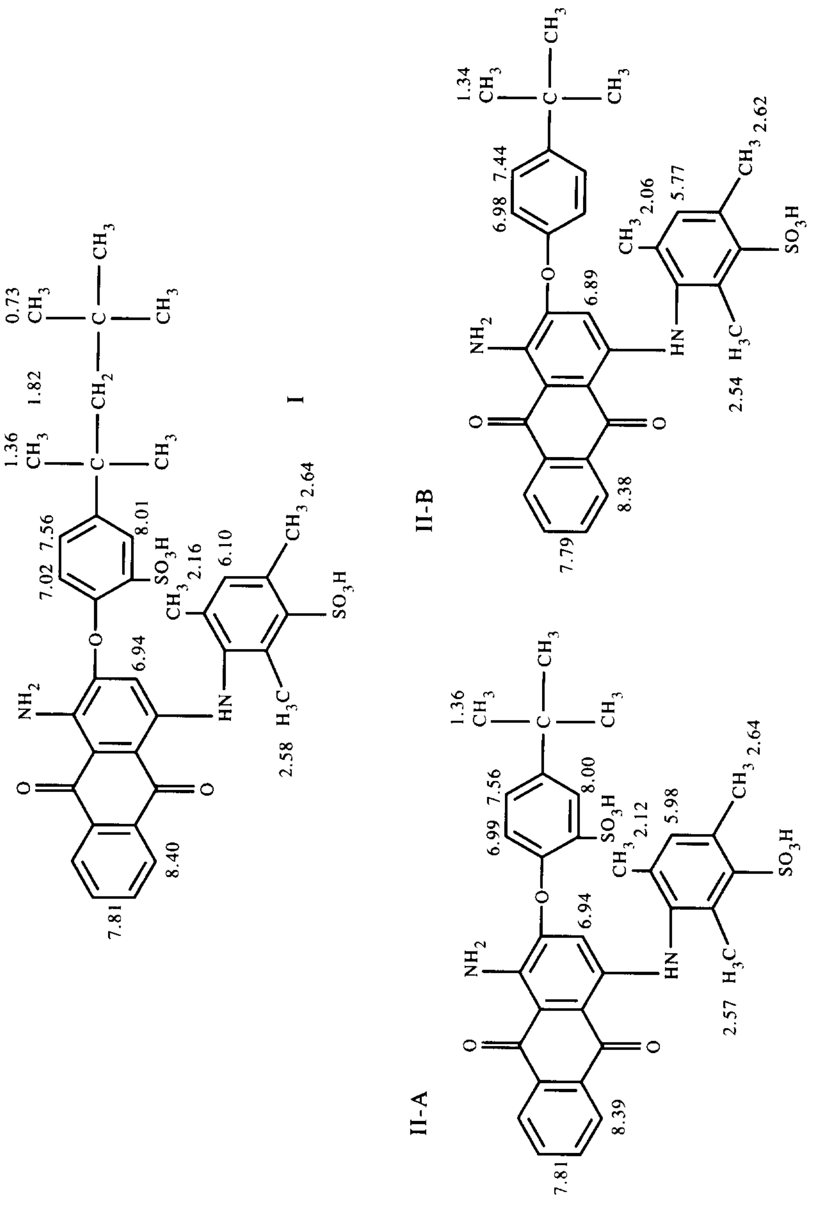


Fig. 2. Chemical shifts of dyes I and II.

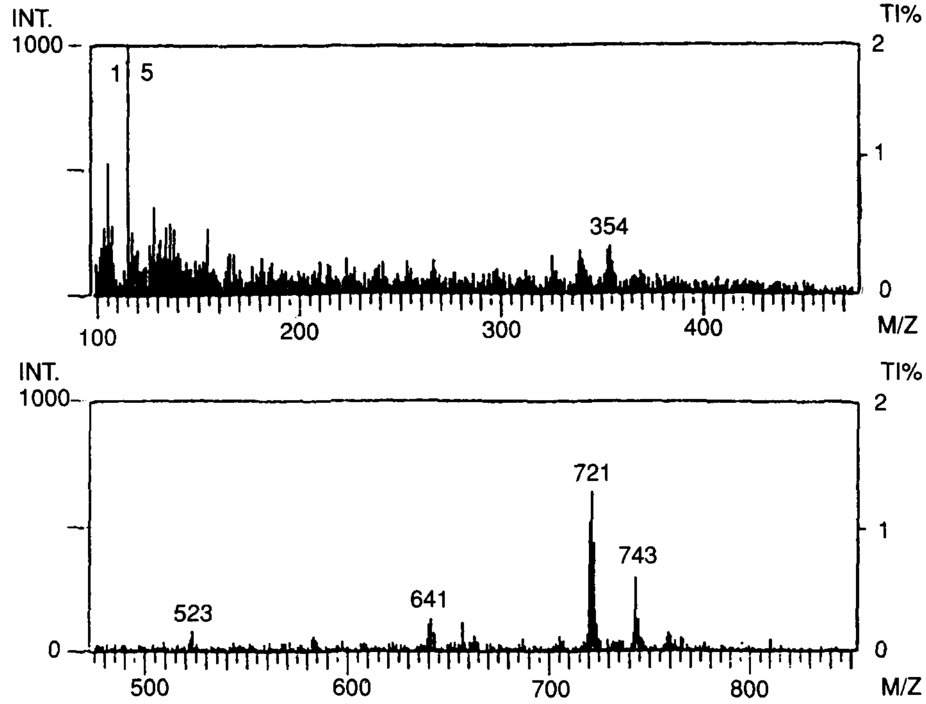


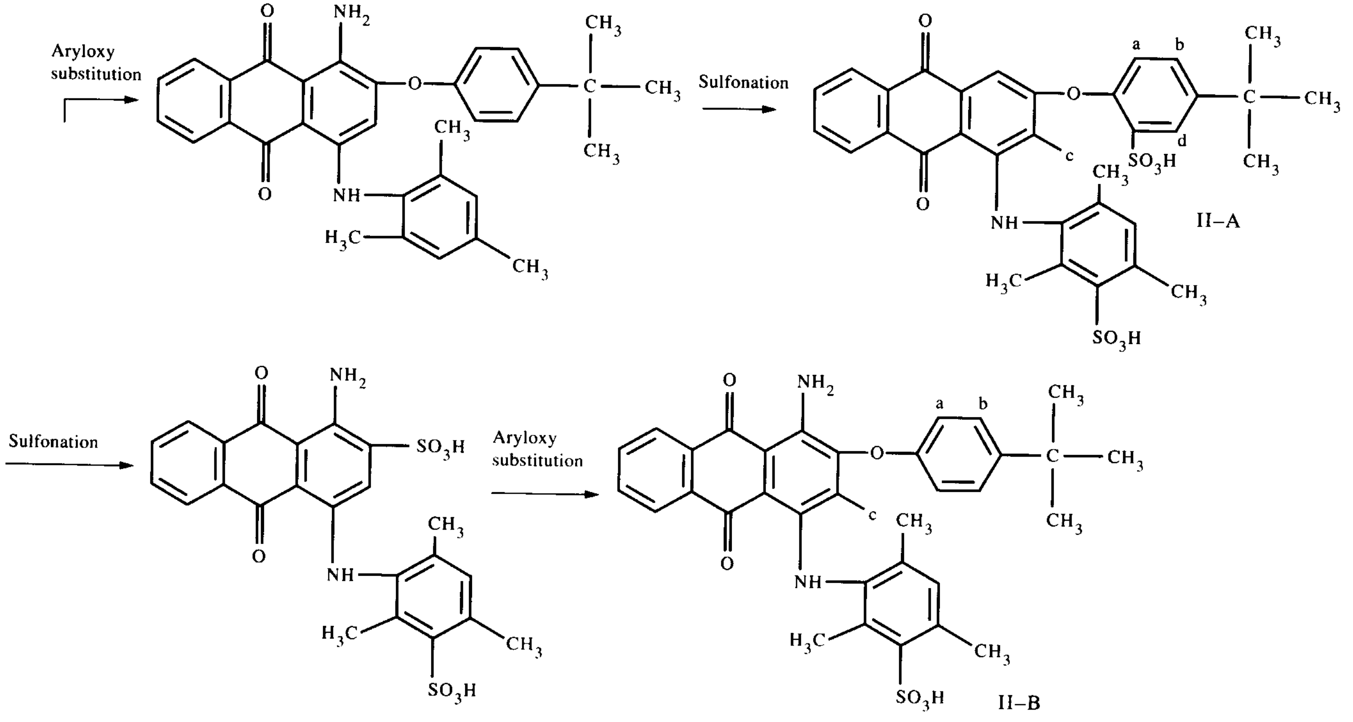
Fig. 3. Mass spectrum of dye I.

Structure determination

In order to define the structural formula of the synthesized dyes, dyes **II-A** and **II-B** were prepared *via* different synthetic routes, as outlined in Scheme 1, and the ^{1}H-NMR of both dyes were determined; data are shown in Table 2.

Dye **II-B** was prepared by initial sulfonation, and then aryloxy substitution; the sulfonic acid group could not be introduced to the aryloxy residue. The numbers of protons on the a- and b-positions corresponded to 2, respectively, as deduced from the area of peaks. Dye **II-A** was prepared by initial aryloxy substitution and then sulfonation.

With respect to the ^{1}H-NMR spectra of dye **II-A**, the chemical shifts of the protons on the a- and c-position (e.g. the 3-position of the anthraquinone moiety) were very close, and the total number of protons on both positions was 2.3. The proton integration on the 3-position of the anthraquinone moiety was 1. Thus the number of protons on the a-position must be in the region of 1 to 2. The sulfonic acid group was introduced in the a-position of the aryloxy residue, it can be seen that the number of sulfonic acid groups on the a-position must be in the range of 0 to 1 ($0<n<1$). In addition, the



Scheme 1. Synthetic processes.

TABLE 2
^{1}H-NMR Data

Dye no.	*Recorded no.*	*Shift*	*Area of peak*	*Rate of area of peak*	*Number of proton*
II-A	c	6.94			1
	a	6.99	0.8609	2.3	1<2
	b	7.56	0.3698	1	1
	d	8.00	0.5820*	1.6	1
II-B	c	6.89	0.3737	1	1
	a	6.98	0.8381	2.2	2
	b	7.44	0.8571	2.3	2
I	c	6.94			1
	a	7.02	1.295	2.4	1< H <2
	b	7.56	0.714	1	1
	d	8.01	0.774	1.1	1

*There is a bigger peak of impurity.

proton on the b-position between the sulfonic acid group and the alkyl group was significantly affected by the sulfonic acid group, so that the chemical shift of this proton is displaced to 8.00 ppm.

The structure of dye **I** can be similarly deduced (Fig. 2 and Table 2).

As a result, the general formula of the dyes prepared in this investigation can be shown as in Fig. 4.

In the MS spectra of dye **I** (Fig. 3) m/e: 743, 721 and 641 peaks suggested the molecular ions of the mono-sodium disulfonate, disulfonic acid and monosulfonic acid, respectively. Thus, it is clearly apparent that the title dyes were a mixture of mono- and di-sulfonic acid.

Influence of structure on colour

As is well established, the colour of acid dyes derived from bromaminic acid and arylamines encompasses various blue hues. With regard to the influence

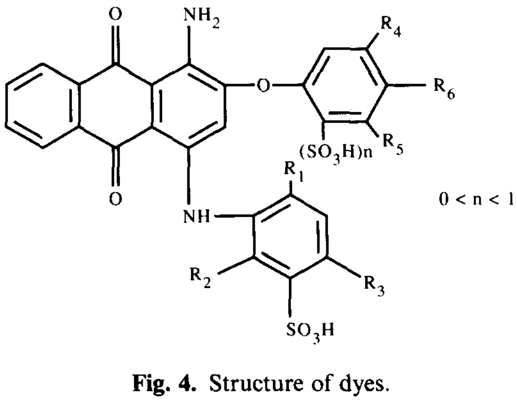


Fig. 4. Structure of dyes.

of structure on the colour of the dyes, it can be concluded that coplanarity of the 4-arylamino group with the anthraquinone ring system is a key factor, relative to the donor properties of the 4-arylmanino substituent [8].

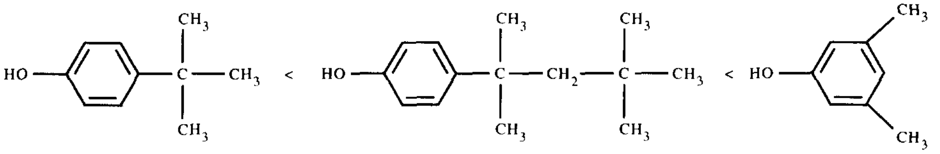
With replacement of the 2-bromo or sulfonic acid group in 1,4-diamino anthraquinone derivatives by an aryloxy group, the colour of the dyes is shifted from a blue to violet hue [4,6,12,13]. The introduction of electron donor substituents (e.g. an aryloxy group) into the 2-position of dyes based 1,4-diaminated anthraquinone produces a hypsochromic shift.

Visible absorption maxima of dyes **I**–**VI** are given in Table 1. It is apparent that variations of the 2-aryloxy substituents produced only negligible colour shift. For dyes **I**, **II** and **III** λ_{max} shifted about 3 nm, and for dyes **V** and **VI** about 10 nm.

Dyeing experiments were carried out and colours of the wool dyeings were measured in accord with ISO. Data are listed in Table 3. The results indicate that relative to dye **I** as standard, the ΔH values are −1.2178, −0.5181 for dyes **II** and **V**, and 0.6162, 2.4090, 13.1999 for dyes **III**, **VI** and **IV**, respectively, i.e. there is a bathochromic effect in the following sequence.

II < **V** < **I** (bluish–violet) < **III** < **VI** < **IV** (reddish blue).

The various aryloxy substituents affected the colour of the dyes in the sequence as below:



Dyeing properties of the dyes

The six acid violet dyes were evaluated for the dyeing of wool using established procedures; representative fastness of the dyeing are listed in Table 4.

TABLE 3
Colour Parameters of the Dyes

Dye no.	I	II	III	IV	V	VI
L	26.6766	26.8518	25.2187	20.5453	26.3839	25.2905
A	28.1914	29.1576	27.2218	12.4436	23.0097	23.1259
B	−39.4850	−39.0557	−39.0074	−30.3013	−31.6190	−35.4521
C	48.5162	48.7392	47.5668	32.7569	39.1051	42.3280
h	305.5259	306.7437	304.9097	292.3260	306.0440	303.1169
ΔH	—	−1.2178	0.6162	13.1999	−0.5181	2.4090
ΔC	—	−0.2230	0.9494	15.7593	9.4111	6.1882
ΔE	—	1.1805	1.8149	19.2335	9.4229	6.5111

TABLE 4
Fastness Properties of the Dyes

Dye no.	**I**	**II**	**III**	**IV**	**V**	**VI**
Light (1/1 depth)	7	6.5	6	5.5	6	6
Washing soap	4.5	4.5	4.5	4.0	4.0	4.5
Wool staining	4.5	4.5	4.5	4.5	4.5	4.5
Cotton staining	5.0	5.0	5.0	4.5	4.5	4.5
Perspiration	5.0	4.5	4.5	4.5	4.5	4.5
Wool staining	4.0	4.5	4.0	3.5	3.5	4.0
Cotton staining	4.5	4.0	4.0	4.0	4.0	4.5
Rubbing dry	4.5	4.5	4.5	4.0	4.5	4.5
wet	4.5	4.0	4.5	3.5	4.5	4.5
Dye uptake (1%)	97	86	83	75	89	94

All the dyes had excellent colouration properties on wool, silk and synthetic polyamide, giving intense brilliant bluish violet shades. Dye **IV** gave a reddish blue colour and all dyeings had very good fastness to light wet treatment rubbing and high dye uptake (except for dye **IV**).

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