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Monoazo dyes based on 5,10-dihydrophenophosphazine, Part 2: Azo acid dyes

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ABSTRACT

2-Amino-5,10-dihydro-10-hydroxyphenophosphazine 10-oxide, a non-mutagenic aromatic amine, was diazotized and combined with various sulfonated naphthalene-based coupling components to give new monoazo dyes, the structures of which were confirmed using mass spectrometric and NMR analyses. Investigation of the properties of the target colorants as acid dyes indicated that they furnished deep shades on wool and silk; those dyes containing only one sulfonic acid group gave black shades on wool at 3% omf depth of shade whilst three of these dyes gave bluish-black shades and one gave a reddish-black shade on wool. The black color of the four shades was similar to that obtained using C.I. Acid Black 1 and the resultant fastness properties were generally good.

1. Introduction

Azo dyes constitute the largest group of synthetic dyes both in number and in commercial volume [1,2]. They are relatively economical to produce and have high color strength. While they are used most often to add color to textiles, paper, leather, food, drug and cosmetic products, they are also used in high-tech applications involving dye lasers, thermal transfer printing, fuel cells, and liquid crystal displays [3].

In some azo dyes, the azo linkage undergoes reductive-cleavage by reductase enzymes in mammalian systems [4,5] to give carcinogenic aromatic amines (Fig. 1). This process produces the aromatic amine, which is used as the diazo component and the aminated derivative of the coupler. This indicates that commercial dyes derived from a carcinogenic amine can be free of the parent amine as a contaminant and still be genotoxic. Therefore, color chemists worldwide are cognizant of the need to use eco-friendly (e.g. non-mutagenic) aromatic amines in dye synthesis, taking special care to identify substitutes for the human carcinogens benzidine and β-naphthylamine [6–9]. In this regard, it is known that the presence of sulfonic acid groups in the diazo component removes the potential for genotoxicity in the reductive-cleavage product. However, too many sulfonic acid groups in the dye structure have adverse effects on wet fastness.

With the above principles in mind, Bello and co-workers reported that diamino derivatives of the 5,10-dihydrophenophosphazine system were potential substitutes [10–15] for benzidine in the formation of analogs of certain benzidine-based azo direct dyes that are now banned [12]. The present paper is concerned with the synthesis and properties of 2-amino-5,10-dihydro-10-hydroxyphenophosphazine 10-oxide (**4**) and its use as a diazo component in the synthesis of novel monoazo acid dyes (**D$_1$**–**D$_6$**) based on the naphthalene system (Fig. 2). The spectroscopic properties and utility of these new dyes for dyeing wool and silk were studied.

2. Experimental methods

All reagents were commercial products of analytical grade. 5,10-Dihydro-10-hydroxy-2-nitrophenophosphazine 10-oxide was obtained *via* nitration of 5,10-dihydro-10-hydroxyphenophosphazine 10-oxide using a mixture of HOAc and concentrated HNO_3 and according to a reported method [16]. Melting points were determined with a Mel-Temp capillary melting point apparatus (Shanghai, China) and are uncorrected. IR spectra were obtained using an FT/IR-430 spectrophotometer (JASCO Ltd. Co., Japan). HPLC analyses were performed using an HP1050 Liquid Chromatography (HEWLETT PACKARD Ltd. Co., USA). Mass spectra were recorded at CID = 50–200 V with an HP1100 HPLC/MS system (HEWLETT PACKARD Ltd. Co., USA). NMR spectra were obtained on a Varian INOVA 400 MHz spectrophotometer (Varian INOVA Ltd. Co., USA) using DMSO-d_6 as solvent, TMS as the internal standard for ^{1}H and ^{13}C spectra and 85% H_3PO_4 for ^{31}P spectra. For coupling constants, ^3J and ^4J refer to three-bond

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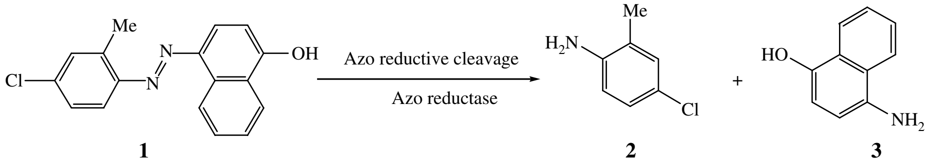


Fig. 1. Reductive-cleavage of an azo dye via azo reductase.

coupling constants from ^1H–^1H or ^{31}P–^1H and four-bond coupling constants from ^{31}P–^1H or ^1H–^1H, respectively. Colorimetric data were recorded using an Ultra Scan Xe electron color-matching photometer (Hunter Ltd. Co., USA), using illuminant D65, 100 standard observer with specular component excluded; in this context, the terms EP and Dom WL refer to purity of color and dominant wavelength. Each sample was measured four times and the data averaged. For fastness assessments, wash fastness of the dye samples was tested according to ISO 105-C01:1989 using an S-1002 two bath dyeing and testing apparatus (Roaches Co., UK), perspiration fastness according to ISO 105-E04:1994 using a YG(B) 631 perspiration fastness testing apparatus and Y902 perspiration fastness testing oven (Darong Standard Textile Apparatus Co. Ltd., Wenzhou), and light fastness according to ISO 105-B02:1994 using a Xenotext 150-S Weatherometer (Heraeus Co., Germany). The proprietary cationic fixative, *fixing agent Y*, was obtained from Kaifeng Oil Chemicals in China, as a 45.5% solid composition. A commercial sample of C.I. Acid Black 1 was provided by Henan Chengtai Chemical Technology Co., Ltd. in China. The scoured, woven silk (105 gm^{-2}) and wool (125 gm^{-2}) fabrics used in this study were obtained from the Standardization Institute of China Textile Industry.

2.1. Synthesis of intermediates

*2.1.1. 5,10-Dihydro-10-hydroxy-2-nitrophenophosphazine 10-oxide (**5**)*

Compound **5** was prepared in 74% yield using a reported method [16]. The product had mp >300 °C (dec); IR (KBr) ν: 3261, 3162, 2286, 1529, 1350, 1167, 1130, 959; MS (CID = 100 V) m/z (% rel. int.): 276.2 ($[M]^+$, 100), 229.1 ($[M - HNO_2]^+$, 28); ^1H NMR δ: ~4.8 (broad peak), 7.20 (t, 1H, $^3J = 7.2, 6.7$), 7.27 (t, 1H, $^3J = 7.4$, $^4J_{P\text{–}H} = 6.3$), 7.31 (q, 1H, $^3J = 9.2$, $^4J_{P\text{–}H} = 6.0$), 7.55 (q, 1H, $^3J = 6.7, 7.4$), 7.78 (q, 1H, $^3J = 7.2$, $^3J_{P\text{–}H} = 12.7$), 8.25 (q, 1H, $^3J = 9.2$, $^4J = 2.5$), 8.56 (q, 1H, $^4J = 2.5$), 10.80 (s, 1H); ^{13}C NMR δ: 114.9, 115.8, 116.9, 120.0, 121.5, 125.8, 126.4, 128.4, 132.1, 139.1, 141.1, 146.8; ^{31}P NMR (DMSO-d_6, 85% H_3PO_4) δ: 9.2.

*2.1.2. 2-Amino-5,10-dihydro-10-hydroxyphenophosphazine 10-oxide (**4**)*

To an autoclave (150 mL) were added MeOH (50 mL) and compound **5** (2 g). The reaction mixture was adjusted to pH 7.0–7.2 using 5–10% KOH in MeOH (w/w). After adding 5% Pd/C (0.12 g), compound **5** was hydrogenated at 0.6–0.8 MPa and 65 °C for 10 h and the reaction mixture was cooled to room temperature. The catalyst was removed by filtration and the filtrate was adjusted to pH < 3.5 using 36% HCl, whereupon a flaky silver precipitate formed. The solid was collected by filtration and washed with cold water to give 1.3 g **4** (70%). MS (CID = 50 V) m/z (% rel. int.): 245.2 ($[M - H]^-$, 100), 491.9 ($[M_2 - H]^-$, 20); ^1H NMR δ: ~4.6 (broad peak), 6.82 (q, 1H, $^3J = 8.8$, $^4J = 2.2$), 6.91 (t, 1H, $^3J = 6.9, 6.3$), 6.93 (q, 1H, $^3J = 8.8$, $^4J_{P\text{–}H} = 6.8$), 6.99 (d, 1H, $^4J = 2.2$), 7.05 (t, 1H, $^3J = 8.0$, $^4J_{P\text{–}H} = 6.4$), 7.35 (t, 1H, $^3J = 6.3, 8.0$), 7.65 (q, 1H, $^3J = 6.9$, $^3J_{P\text{–}H} = 12.6$), 9.58 (s, 1H); ^{13}C NMR δ: 111.7, 112.6, 114.7, 115.5, 116.9, 118.1, 120.4, 128.7, 131.1, 134.1, 141.2, 143.0; ^{31}P NMR δ: 12.9.

*2.2. Synthesis and purification of dyes **D_1–D_6***

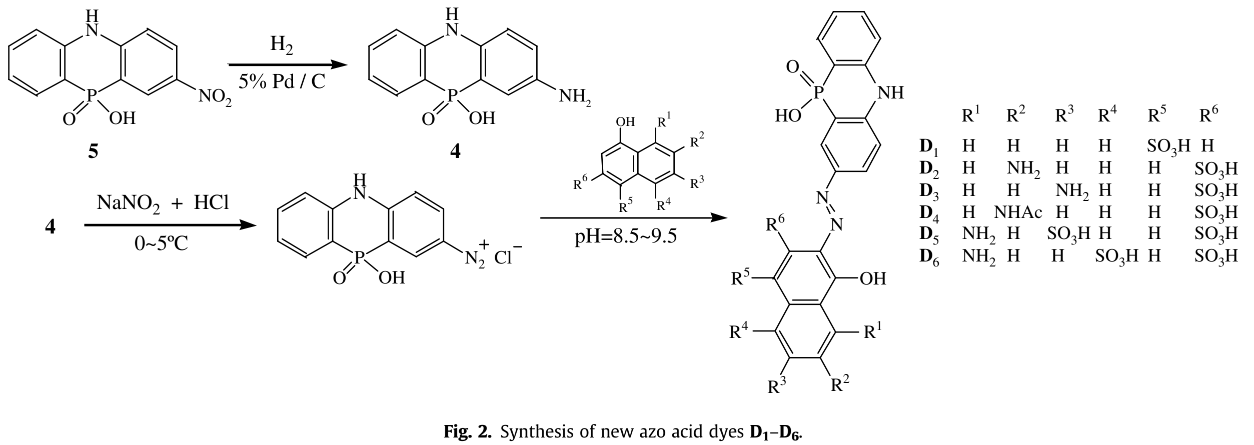
2.2.1. Dye synthesis

To a mixture of water (5 mL) and compound **4** (1 g, 4 mmol) was added Na_2CO_3 (2.3 mL, 10%, w/w), and the reaction mixture was stirred until dissolution occurred. The solution was cooled to 5 °C, and conc. HCl (1 mL, 10–11 mmol) was added followed by $NaNO_2$ (0.28 g, 0.41 mmol) at 0–5 °C. Stirring was continued for ~30 min to give a light brown transparent solution that was allowed to stand at 0–5 °C while the solution of coupler was prepared.

Na_2CO_3 (10%, w/w) was added to a stirred mixture of water (10 mL) and coupling component (4 mmol) until the coupling component was essentially dissolved. After filtering to remove a tiny amount of insoluble material, the colorless solution was adjusted to pH = 8.50–9.50 using Na_2CO_3 (10%, w/w) and cooled to 10–15 °C. The pH was maintained 8.50–9.50 and the temperature at 15 °C as the solution of diazonium salt was added dropwise. The reaction mixture was stirred until the concentration of coupler was <0.02% based on colorimetric analysis (i.e. reaction on filter paper between the diazonium salt obtained from *para*-nitroaniline and the reaction mixture, and comparison with results from a solution containing 0.02% coupler). NaCl (solid) was added to precipitate dye and vacuum drying gave 2.5–3.0 g dyes **D_1–D_6**.

2.2.2. Dye purification

Salt removal and dye purification for all dyes, including C.I. Acid Black 1, were conducted by dissolution and re-precipitation using



	R^1	R^2	R^3	R^4	R^5	R^6
D_1	H	H	H	H	SO_3H	H
D_2	H	NH_2	H	H	H	SO_3H
D_3	H	H	NH_2	H	H	SO_3H
D_4	H	NHAc	H	H	H	SO_3H
D_5	NH_2	H	SO_3H	H	H	SO_3H
D_6	NH_2	H	H	SO_3H	H	SO_3H

Fig. 2. Synthesis of new azo acid dyes **D_1–D_6**.

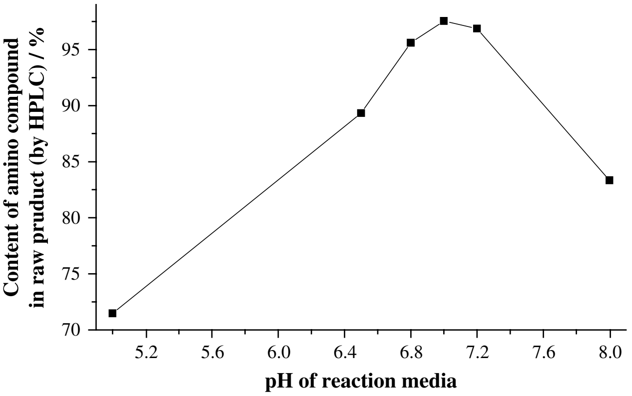


Fig. 3. Effects of reaction pH on the reduction of compound **5** with 6% (w/w) 5% Pd/C.

DMF-ether [17], to give dye contents >90%. The purity of the resultant dyes was checked using paper chromatography [18], with butanol:water:DMF (11:11:3) or butanol:pyridine:water (5:3:5) as eluent.

2.3. Spectrophotometric analyses

Dyes $\mathbf{D_1}$–$\mathbf{D_6}$ (2.0×10^{-5} mol) were dissolved in deionized water (25 mL) with the aid of Na_2CO_3 (5% w/w). A portion of this solution (0.25 mL) was diluted to 25 mL with deionized water and allowed to stand overnight. Absorption spectra were recorded and used to determine λ_{max} values and to calculate molar extinction coefficients of dyes $\mathbf{D_1}$–$\mathbf{D_6}$ according to Beer–Lambert law.

2.4. Determination of dye uptake

2.4.1. Standardized curve

Dye (0.1 g), Na_2SO_4 (0.6 g), fatty alcohol polyoxyethylene surfactant (0.4 g), and water (15 mL) were added to a 50-mL beaker and the solution was stirred or sonicated. The pH was adjusted to 3–4 with aq. acetic acid and the solution was diluted to 100 mL using deionized water. A portion of this dye solution (0.1–0.8 mL) was placed in eight 25-mL volumetric flasks and the volume of each was adjusted to 25 mL using deionized water. Absorbance (A_i) values were determined for each solution at λ_{max} as a function of dye concentration.

2.4.2. Dye uptake measurements

Stock dye solutions prepared above (80 mL) were added to a 100-mL three-necked flask, deionized water (10 mL) was added, and the pH was adjusted to 3–4 using aq. acetic acid. The flask was equipped with a mechanical stirrer, thermometer, and a 600 × 4 mm glass cold finger. Either wool or silk fabric (2 g) was added at 25 °C and the time was recorded. Bath aliquots (0.80 mL) were removed and diluted to 25 mL at the following times and temperatures: 5 min/25 °C, 10 min/35 °C, 20 min/40 °C, 40 min/60 °C, 60 min/90 °C, 80 min/95 °C, 120 min/95 °C, 150 min/95 °C, and 180 min/95 °C. Following the removal of each aliquot, Na_2SO_4 (0.80 mL, 20% w/w) was added to the flask to keep the liquor ratio constant. The absorbance (A_i) value of each solution was recorded at λ_{max} and the corresponding dye concentration (C_i) was determined from the standard curve (Table 6) for the corresponding dye.

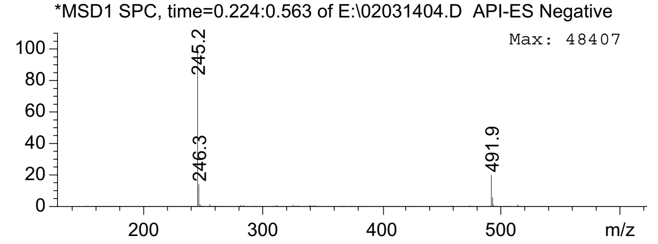


Fig. 5. Negative ion ES-MS of compound **4** at CID = 50 V.

The fabric quantities sufficient for fastness studies were obtained by repeating the dyeing process using 20 g fabric samples.

2.4.3. After-treatments

The dyed fabric samples were rinsed with cold water and treated for 30 min at 50–60 °C with a solution containing *fixing agent Y* (7.5% omf) and aq. acetic acid (2 mL), at a 30:1 liquor ratio. The dyed fabrics were rinsed, air-dried and ironed.

2.5. Fastness assessments

2.5.1. Wash fastness

Dyed and after-treated fabric samples (100 × 40 mm) were attached to the same size undyed woven wool and cotton fabric samples and immersed in a bath of 0.5% detergent at 40 °C and at a liquor ratio of 50:1. After 30 min, the samples were removed, briefly rinsed twice with distilled water, rinsed for 10 min with tap water, and air dried below 60 °C. Changes in shade and staining of adjacent fabrics were evaluated with the aid of grey scales for color change and transfer.

2.5.2. Perspiration fastness

Dyed wool–undyed wool and dyed wool–undyed cotton fabric combinations mentioned in Section 2.5.1 were immerged in pH 8 solution containing 0.5 g/L L-histidine hydrochloride, 5 g/L NaCl, 2.5 g/L $Na_2HPO_4 \cdot 2H_2O$ and in a pH 5.5 solution containing 0.5 g/L L-histidine hydrochloride, 5 g/L NaCl, 2.2 g/L $NaH_2PO_4 \cdot 2H_2O$ for

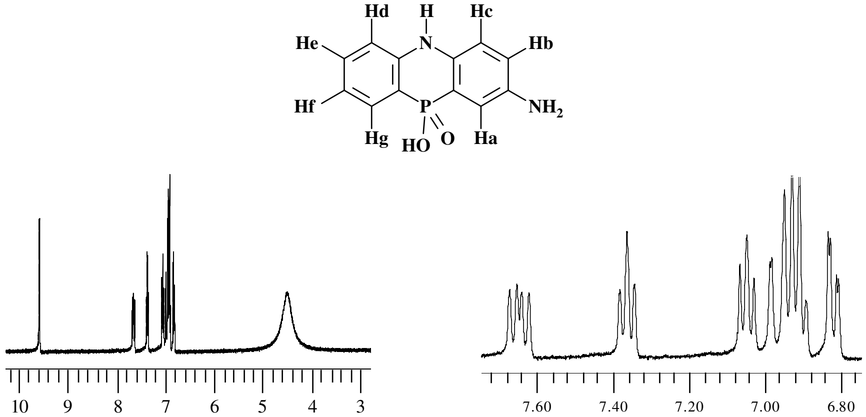


Fig. 4. ^1H NMR (400 MHz) spectrum of compound **4** in DMSO-d_6.

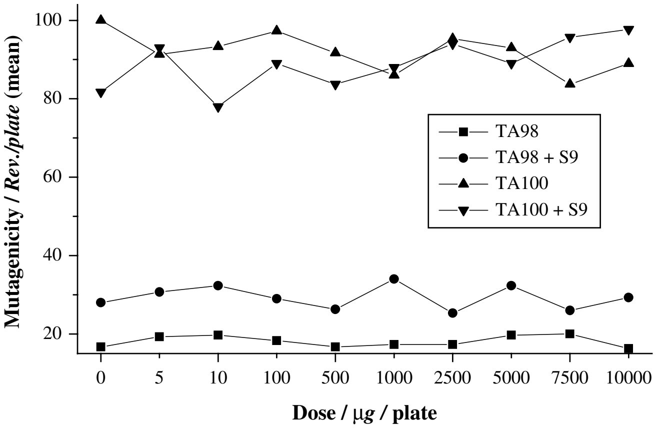


Fig. 6. Mutagenicity of compound **4** with and without *S9* metabolic activation [21].

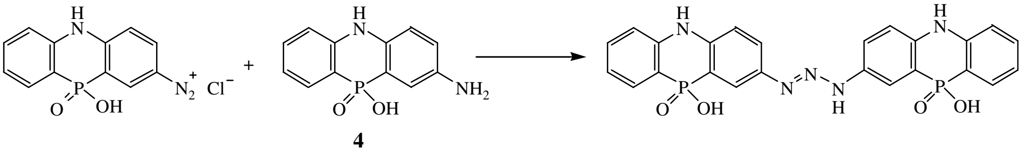


Fig. 7. Side reaction between arylamine **4** and corresponding diazo compound.

Table 1
API ES-MS data for dyes $\mathbf{D_1}$–$\mathbf{D_6}$.

Dyes	M ions		M/2 ions		M/3 ions	
	Peaks and assignments	%Rel. int.	Peaks and assignments	%Rel. int.	Peaks and assignments	%Rel. int.
$\mathbf{D_1}$	479.8(M − H)	100	239.4(M − 2H)	23	—	—
$\mathbf{D_2}$	494.7(M − H), 516.7(M + Na − 2H)	28, 37	246.9(M − 2H)	100	—	—
$\mathbf{D_3}$	494.6(M − H)	100	268.7(M + 2Na − 4H)	13	—	—
$\mathbf{D_4}$	558.7(M + Na–2H), 559.7(M + Na − 2H), 536.7(M − H)	27, 9, 8	267.9(M − 2H)	100	—	—
$\mathbf{D_5}$	618.9(M + 2Na − 3H)	4	298.0(M + Na − 3H), 286.9(M − 2H)	53, 29	190.9(M − 3H)	100
$\mathbf{D_6}$	575.6(M − H), 597.6(M + Na − 2H)	7, 6	298.5(M + Na − 3H), 287.3(M − 2H)	18, 100	191.2(M − 3H)	42

30 min at a 50:1 liquor ratio. The samples were removed, placed between a pair of glass plates, squeezed at 12.5 kPa pressure to remove most of the liquid, incubated in an oven at 37 ± 2 °C for 4 h, and air-dried below 60 °C. Changes in shade and staining were evaluated using the standard grey scale rating.

2.5.3. Light fastness assessments

Dyed fabrics were irradiated in a commercial xenon arc weatherometer until the change in shade of #**6** and #**7** blue-standard fabrics reached the **4–5** levels using the grey scale. The exposure parameters were: black panel temperature = 50 °C, 1500 W, filter inner/outer = quartz/glass, irradiance = 42 W/m^2 at 300–400 nm. Light fastness values for dyes $\mathbf{D_1}$–$\mathbf{D_6}$ were based on shade depth differences between unexposed and irradiated fabrics.

Table 2
Spectral properties of dyes $\mathbf{D_1}$–$\mathbf{D_6}$.

Dyes	λ_{max} (nm)	$\varepsilon_{max} \times 10^4$ (L mol cm^{-1})
$\mathbf{D_1}$	561	1.9
$\mathbf{D_2}$	568	2.8
$\mathbf{D_3}$	546	2.6
$\mathbf{D_4}$	569	3.0
$\mathbf{D_5}$	581	2.4
$\mathbf{D_6}$	592	2.8
AB-1[a]	593[b]	2.7

[a] C.I. Acid Black 1.
[b] Spectrum also has small peak at 450 nm.

3. Results and discussion

3.1. Synthesis of compound *4*

Following the preparation of aromatic amino compounds, when the compound **5** (5,10-dihydro-10-hydroxy-2-nitrophenophosphazine 10-oxide), a dark yellow intermediate, was reduced over 5% Pd/C at pH 5, 0.75 ± 0.05 MPa, and 65 °C for 10 h, approximately 28% of the starting nitro compound was found in the crude product, even when 10% (w/w) catalyst was used. The reason for using acidic conditions was to trap the product as the HCl salt as it formed. An investigation into the nature of this step showed that the nitro compound could be essentially fully reduced at neutral pH and that the amount of catalyst played an important role in the hydrogenation process. For example, when the amount of 5% Pd/C was less than 6% (w/w) of the nitro compound, the crude reduction product always contained a small amount of the starting nitro compound that disappeared once the amount of 5% Pd/C reached 6% (w/w). It was noted that the pH of reaction media also played an important role in the hydrogenation process. For example, the results in Fig. 3 showed that the proportion of the target amine reached a maximum at pH 7, only to drop again once the pH became alkaline.

Following recrystallization of compound **4** from ethanol, its chemical structure was confirmed by NMR (Fig. 4), MS (Fig. 5), and IR analyses. API ES-MS showed [M − H] at *m*/*z* 245 as the base peak in the spectrum. The NMR spectrum showed the expected multiplet for H-g at δ 7.65–7.8 owing to H–H coupling with H-f and P–H couplings with the phosphorus atom. Other notable and well-resolved signals were triplets for H-e and H-f (δ 7.3 and 7.15, respectively), and a doublet of doublets for H-b (δ 7.05).

3.2. Mutagenicity of compound *4*

Compound **4** was purified using flash column chromatography [19] until its purity level exceeded 98%, and was evaluated for mutagenicity in the standard *Salmonella*/mammalian microsome assay, with and without *S9* metabolic activation [20]. The results indicated that this amine was non-mutagenic in bacteria strains TA98 and TA100 (Fig. 6 [21]), in the presence and absence of *S9* activation. In each case, there was little difference between the number of revertant colonies when TA100 was used, and in TA98 less than a two-fold increase in revertant colonies was found.

Table 3
Shades and fastness properties for dyes $\mathbf{D_1}$–$\mathbf{D_6}$ on wool and silk.[a]

Dyes	Shade on wool (silk)	Light fastness	Wash fastness		
			Change in shade	Staining on cotton	Staining on wool
$\mathbf{D_1}$	Reddish black (Blue purple)	4–5 (4)	4–5 (4)	4 (1–2)	4–5 (2)
$\mathbf{D_2}$	Reddish black (Dark purple)	>6 (4)	4 (4)	2–3 (3)	4 (4)
$\mathbf{D_3}$	Reddish black (Purple)	3–4 (3)	4–5 (4)	4 (3)	4–5 (4–5)
$\mathbf{D_4}$	Reddish black (Reddish purple)	5–6 (4)	4–5 (4–5)	3 (2)	4–5 (4)
$\mathbf{D_5}$	Reddish black (Navy blue)	4 (3)	4–5 (4)	3 (3)	4 (4)
$\mathbf{D_6}$	Navy blue (Reddish blue)	4 (3)	4–5 (3)	2 (4)	4 (4–5)
AB-1[b]	Greenish black (Greenish blue)	4 (2–3)	4–5 (3)	2–3 (3)	4 (3–4)

[a] Data in parentheses are from silk samples at 5% (omf).
[b] C.I. Acid Black 1.

Table 4
Perspiration fastness for dyes $\mathbf{D_1}$–$\mathbf{D_6}$ on wool and silk.[a]

Dyes	Acidic pH			Alkaline pH		
	Change in shade	Staining on cotton	Staining on wool	Change in shade	Staining on cotton	Staining on wool
$\mathbf{D_1}$	4–5 (4–5)	2 (2)	3 (2–3)	4–5 (4–5)	2–3 (1–2)	3 (2)
$\mathbf{D_2}$	4–5 (4–5)	2 (2)	2–3 (3)	4–5 (4–5)	1–2 (1–2)	2–3 (3)
$\mathbf{D_3}$	4–5 (4–5)	2 (1–2)	3 (3–4)	4–5 (4–5)	2 (2)	2–3 (3)
$\mathbf{D_4}$	4–5 (4)	3 (1)	4–5 (2)	4–5 (4)	1–2 (1)	2–3 (2–3)
$\mathbf{D_5}$	4–5 (4–5)	2 (1–2)	3 (3)	4–5 (4–5)	3–4 (1–2)	3–4 (2–3)
$\mathbf{D_6}$	4–5 (3–4)	3–4 (3)	3 (3–4)	4–5 (3)	2 (1–2)	3 (2–3)
AB-1[b]	4–5 (3–4)	2 (2)	3 (3–4)	4–5 (4)	2 (1–2)	2–3 (2–3)

[a] Data in parentheses were obtained from the silk samples at 5% (omf).
[b] C.I. Acid Black 1.

3.3. *Dye synthesis*

Since compound **4** did not dissolve well in water, an attempt was made to prepare the corresponding diazo compound using the reverse order mode of diazotization [22]. Using this method, varying amounts of a diazoamino compound [23] formed, as a dark brown precipitate, from a reaction between the diazo intermediate and starting amine (Fig. 7). In order to avoid self-condensation during the diazotization step, compound **4** was dissolved in dilute NaOH and the solution was acidified, precipitating the amine as fine particles which proved to be easily diazotized by HNO_2. The resultant diazonium salt was coupled with six naphthalene-based coupling components at pH 8.5–9.5 to give the target monoazo dyes $\mathbf{D_1}$–$\mathbf{D_6}$.

3.4. *Mass spectral and absorption properties of dyes* $\mathbf{D_1}$–$\mathbf{D_6}$

Results from ES-MS analysis of dyes $\mathbf{D_1}$–$\mathbf{D_6}$ are given in Table 1. The signals observed in the various spectra were consistent with M, M/2, and M/3 ions. Except for $\mathbf{D_1}$ and $\mathbf{D_3}$, the title dyes did not exhibit intense signals for the $[M-H]^-$ ion. Dyes $\mathbf{D_2}$, $\mathbf{D_4}$, and $\mathbf{D_6}$ gave M/2 ions as base peaks, while $\mathbf{D_5}$ gave an M/3 ion as the base peak. All dyes gave a readily detected M/2 peak.

Visible absorption spectra provided the λ_{max} and ϵ_{max} values given in Table 2. It was found that the six new dyes exhibited a bluish hue and absorbed at longer wavelengths than dyes obtained from commonly used aniline derivatives which give reddish hues having λ_{max} values near 500 nm.

3.5. *Dye application*

3.5.1. *Hue and fastness properties*

Wool and silk fabrics were dyed at 3% and 5% omf, respectively; the two fiber types were dyed at different shade depths because of their different structures. The dyed fabrics were treated with 7.5% (w/w) cationic fixing agent (*fixing agent Y*). It was found that dyes $\mathbf{D_1}$–$\mathbf{D_6}$ gave deep shades on both wool and silk and dyes $\mathbf{D_1}$–$\mathbf{D_5}$ gave reddish black on wool at 3% omf (Table 3).

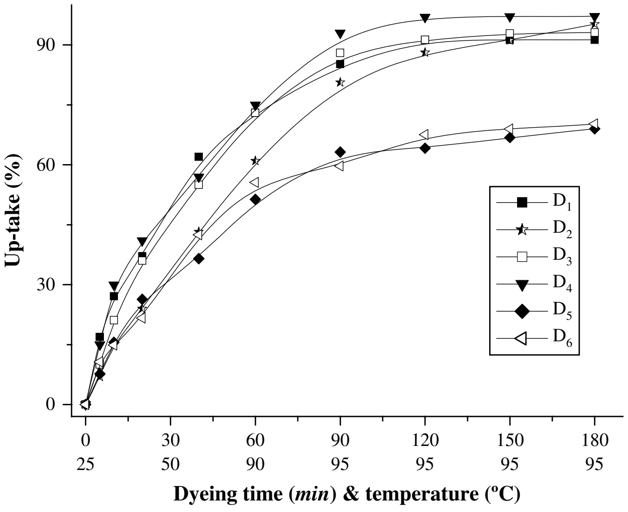


Fig. 8. Uptake of the dyes $\mathbf{D_1}$–$\mathbf{D_6}$ on wool at 3% (omf).

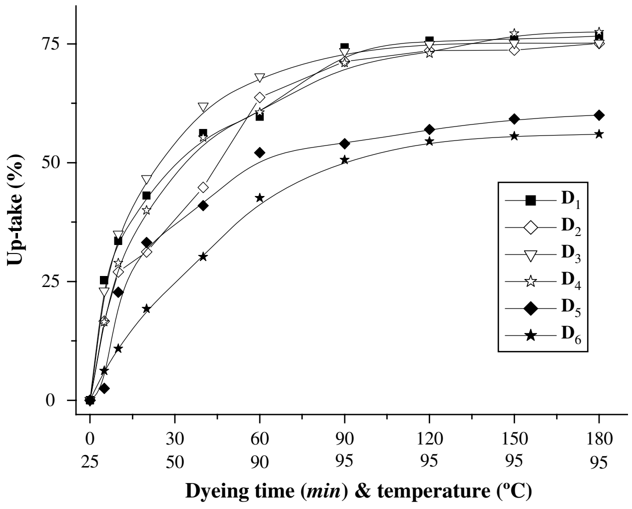


Fig. 9. Uptake of dyes $\mathbf{D_1}$–$\mathbf{D_6}$ on silk at 3% (omf).

Table 5
Tri-stimulus, Dom WL and other color data for dyes $\mathbf{D_1}$–$\mathbf{D_6}$ on wool.

Dyes	*X*	*Y*	*Z*	d*L**	d*C**	d*h**	EP[b]	Dom WL[c]
$\mathbf{D_1}$	1.68	1.69	1.92	13.77	2.27	334.38	5.38	−524.23
$\mathbf{D_2}$	1.58	1.65	1.80	13.52	0.55	322.18	1.37	−545.34
$\mathbf{D_4}$	1.68	1.69	1.85	13.74	2.27	350.07	4.93	−497.39
$\mathbf{D_5}$	1.62	1.66	2.11	13.58	3.28	293.02	8.11	452.52
AB-1[a]	1.73	1.86	2.44	14.71	3.75	258.81	12.39	473.77

[a] C.I. Acid Black 1.
[b] Excitation purity.
[c] Dominant wavelength.

Table 6
Linear equations for dyes $\mathbf{D_1}$–$\mathbf{D_6}$.

Dyes	Linear equations	R^2
$\mathbf{D_1}$	$Y = 0.0110X + 0.0043$	0.9995
$\mathbf{D_2}$	$Y = 0.0064X + 0.0249$	0.9971
$\mathbf{D_3}$	$Y = 0.0088X + 0.0092$	0.9991
$\mathbf{D_4}$	$Y = 0.0155X + 0.0078$	0.9996
$\mathbf{D_5}$	$Y = 0.0094X - 0.0010$	0.9996
$\mathbf{D_6}$	$Y = 0.0162X - 0.0024$	0.9995
AB-1[a]	$Y = 0.061X - 0.0027$[b]	0.9993

[a] C.I. Acid Black 1.
[b] Based on $\lambda_{max} = 593$ nm.

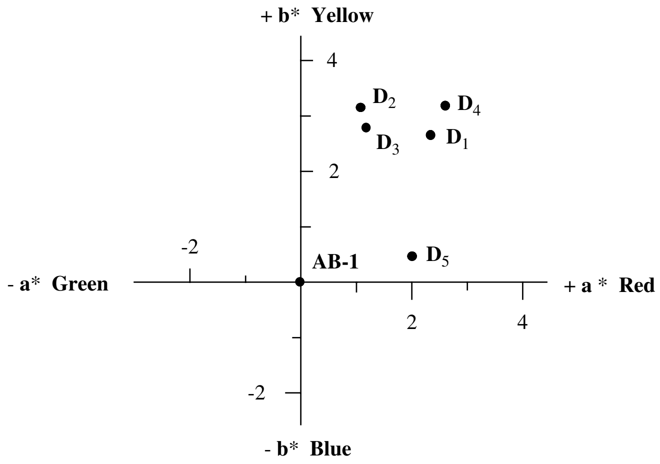


Fig. 10. Positions of dyes $\mathbf{D_1}$–$\mathbf{D_5}$ and Acid Black 1 in CIE 1976 color space.

It was also noted that the title dyes had good light fastness (Table 3) at the depths of shade used, especially when γ-acid type couplers were used (e.g. $\mathbf{D_2}$ and $\mathbf{D_4}$). Wash fastness (Table 3) was slightly better on wool than silk, with no apparent preference for coupler type. Perspiration fastness (Table 4) was very good, with respect to color change, low with respect to staining of cotton or wool. The extent of staining of adjacent wool obtained might be anticipated in view of dye structure; however, one would not expect such small molecules to have substantivity towards adjacent cotton. In addition, it is known that the dihydrophenophosphazine system is not planar [24], which is counterproductive to direct cotton affinity [25].

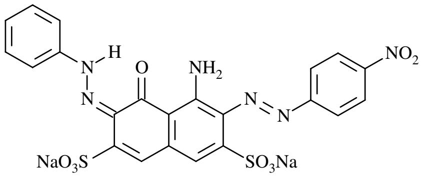


Fig. 11. Molecular structure for C.I. Acid Black 1.

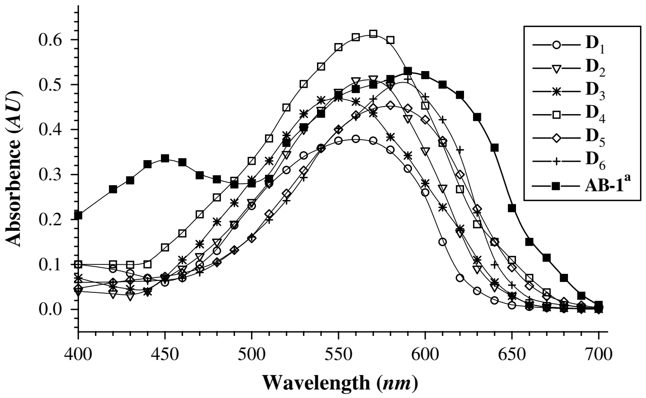


Fig. 12. Visible absorption spectra for dyes $\mathbf{D_1}$–$\mathbf{D_6}$ and C.I. Acid Black 1.

Results from dye uptake on wool and silk indicated that these dyes can be divided into two groups. Group one involved dyes $\mathbf{D_1}$–$\mathbf{D_4}$, which afforded uptake levels up to 90% on wool and 75% on silk; in contrast, the exhaustion of dyes $\mathbf{D_5}$ and $\mathbf{D_6}$ were <75% on wool and <60% on silk (Figs. 8 and 9). Shade differences can be attributed to the higher number of cationic dye sites in wool versus silk [26]. Also, the higher number of sulfonate groups in the latter two dyes allows occupation of multiple dye sites on silk, further limiting the potential shade depths [27]. The higher number of sulfonate groups in $\mathbf{D_5}$ and $\mathbf{D_6}$ also increases dyebath solubility especially at the dyeing temperature, which reduces % exhaustion.

3.5.2. *Colorimetric data for dyes* $\mathbf{D_1}$–$\mathbf{D_6}$

The results shown in Table 5 for wool are consistent with the shades reported in Table 3; the CIE 1976 [28,29] colorimetric data were compared to that obtained using C.I. Acid Black 1 (Figs. 10–12). While there were some differences between the synthesised dyes and C.I. Acid Black 1, the black color of the dyeings was quite similar. It should be noted that the colorimetric data for dye $\mathbf{D_6}$ was not included because the shade obtained was not black.

4. Conclusion

2-Amino-5,10-dihydro-10-hydroxyphenophosphazine 10-oxide, a non-mutagenic aromatic amine, can be used in the synthesis of monoazo acid dyes suitable for dyeing wool and silk fibers. The resultant dyeings afford reddish-black shades on wool having comparable color values to the commercial dye C.I. Acid Black 1. The title dyes are more suitable for dyeing wool than silk, as the dyed wool had better overall fastness properties.

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