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Dyes and Pigments 46 (2000) 121–128

DYES and PIGMENTS

Dyes based on 5,10-dihydrophenophosphazine. Part 1: disazo direct dyes

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Received 2 February 1999; received in revised form 15 November 1999; accepted 4 February 2000

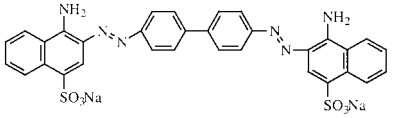
Abstract

The synthesis of 2,8-diamino-5,10-dihydro-10-hydroxy-5-methylphenophosphazine 10-oxide as a possible replacement for the benzidine moiety in some disazo dyes and the use of this new diamine in the preparation of direct dyes were undertaken. The dyes obtained were applied to cotton to give purple to brilliant blue shades, and their structures were confirmed using negative ion electrospray mass spectrometry.

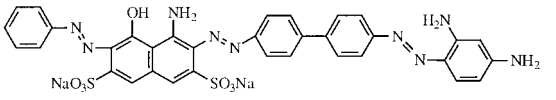
Keywords: Benzidine replacement; Direct dyes; Diaminodihydrophenophosphazine

1. Introduction

It is well known that benzidine is both a mutagenic amine and a human carcinogen [1–4]. Prior to the realization of these facts, many dyestuffs were produced that employed benzidine or a benzidine congener such as *ortho*-tolidine or *ortho*-dianisidine as a precursor. By the 1980s, however, dyes derived from benzidine (e.g. **1–3**) and certain of its derivatives (e.g. **4–6**) were designated as cancer-suspect agents, and alternatives were sought.



1 Congo Red



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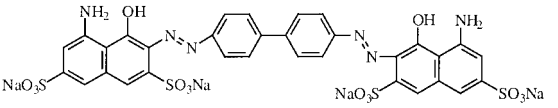
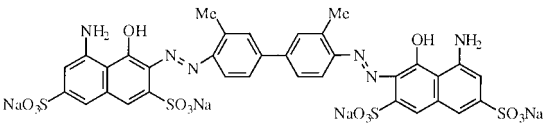


3 C.I. Direct Blue 6



4 C.I. Direct Blue 14 (Trypan Blue)

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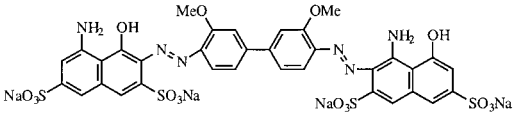
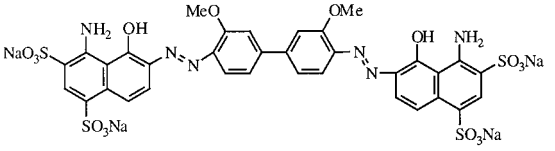
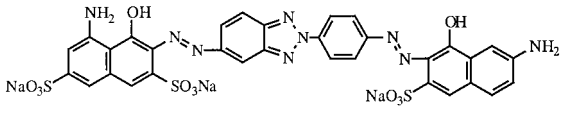


5 C.I. Direct Blue 15

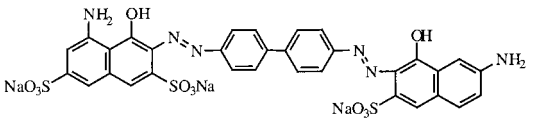


6 C.I. Direct Blue 1

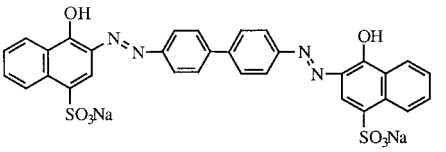
The literature contains several reports concerning attempts to identify suitable benzidine replacements and the conversion of such compounds to dyes. These reports include papers [5,6] that described studies in which dye **7** was synthesized as a possible replacement for dye **8**. Although (**7**) had similar dyeing properties to the prototype, its hue and brightness were slightly different. The benzidine moiety of Congo Red (**1**), Direct Violet 43 (**9**), Direct Black 29 (**10**) and Direct Black 38 (**2**) has been replaced with diaminobipyridine **11** [6], in studies aimed at nongenotoxic dyes for ink-jet printing. In related studies, type **12** benzidines were shown to be nonmutagenic and suitable for ink-jet dye development [7]. It has also been shown that diamines **13–15** can be used to generate polyazo dyes for cellulosic substrates.



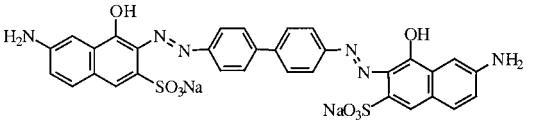
7 Direct Blue 2 analog



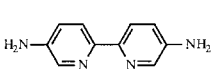
8 C.I. Direct Blue 2



9 C.I. Direct Violet 43



10 C.I. Direct Black 29



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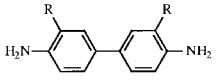
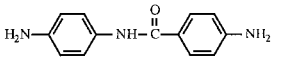


12 R = $C_{3\text{-}4}$ alkyl, alkoxy



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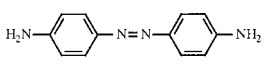

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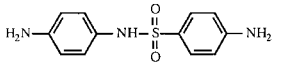

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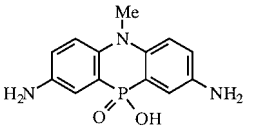
The present paper is concerned with the synthesis of 2,8-diamino-5,10-dihydro-10-hydroxy-5-methylphenophosphazine 10-oxide (**16**) as a possible benzidine replacement for disazo dye development. This ring system has not participated in the current success of heteroaromatic amines, in spite of the published low toxicity and potential therapeutic utility of a number of related compounds. In addition to synthesizing compound **16**, we used it to prepare several disazo dyes and evaluated their properties.



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2. Experimental

2.1. 5,10-Dihydro-10-hydroxyphenophosphazine 10-oxide (**20**)

A mixture of diphenylamine (120 g, 0.72 mol) and PCl_3 (108 g, 0.78 mol) was stirred at room temperature for 20 min and then heated at 210–220°C for 6 h. The viscous oil was cooled to 150°C and water (200 ml) was added. After standing overnight, the resultant brown solid was dissolved in hot ethanol and filtered hot to remove insoluble components. The filtrate was concentrated to give an off-white solid that was air-dried. The solid (**19**) was dissolved in hot HOAc (650 ml) and cooled as a mixture of H_2O_2 (100 g) and HOAc (185 ml) was added. The solution was heated on a steam bath for 30 min, cooled and made alkaline with 10% NaOH. The precipitated solid was removed by filtration and the filtrate was acidified with conc. HCl to give **20** (60 g, 37%). Recrystallization from 95% EtOH gave m.p. 270–272°C (lit. [8] 274–275°C).

2.2. 5,10-Dihydro-10-hydroxy-5-methylphenophosphazine 10-oxide (**21**)

Compound **20** (31.6 g, 0.137 mol) was stirred with DMF (300 ml) for 10 min at 120°C. After cooling the reaction mixture to 33°C, NaH (13.67 g 60% solids) was added, turning the reaction mixture green. When hydrogen evolution ceased, MeI (12.4 ml, 0.199 mol) was added, and the mixture was stirred under reflux for 2 h. After standing overnight at room temperature, the mixture was filtered and the beige solid was re-dissolved in H_2O (400 ml). The filtrate was treated with 3.5 g of charcoal at 60°C for 45 min and acidified using conc. HCl. The product was collected by filtration and washed with water to give 20.21 g (60%), m.p. 252°C (lit. [9] m.p. 253–254°C).

2.3. 5,10-Dihydro-10-hydroxy-5-methyl-2,8-dinitrophosphazine 10-oxide (**22**)

Compound **21** (10.0 g, 40.8 mmol) was added to a mixture of H_2SO_4 (10 ml) and HNO_3 (100 ml) at a rate such that the temperature remained below 20°C. After stirring at 15–20°C for 6 h, the yellow-orange solution was poured into 1 l ice water. The yellow precipitate was collected by filtration and suspended in MeOH (300 ml). The pH was raised to 8 using methanolic KOH (10%), and the mixture was stirred at the boil with charcoal (1.0 g) for 1 h. After removing the charcoal and allowing the filtrate to cool, the product was obtained as yellow crystals (5.61 g, 41%), m.p. 320°C (dec.), (lit. [9] m.p. >320°C).

2.4. 2,8-Diamino-5,10-dihydro-10-hydroxy-5-methylphenophosphazine 10-oxide (**16**)

Compound **22** (4.2 g, 12.5 mmol) was suspended in 250 ml of MeOH and the pH was adjusted to 7.2 with methanolic KOH (10%). The compound was hydrogenated over 5% Pd/C (420 mg) at room temperature for 6 h under 0.6 mPa pressure. The catalyst was removed, and the light blue solution was acidified using conc. HCl (11 ml) and stirred for 1h at the boil with 2 g charcoal. Removal of the charcoal and solvent gave a solid with a blue-gray tint (**16**.2HCl; 2.92 g, 67%), m.p. >250°C (dec.). Mass spectrum (EI) $M^+ = m/e$ 348 ($C_{13}H_{16}N_3O_2PCl_2$).

2.5. Dye synthesis

Compound **16** (1 g, 3.6 mmol) was dissolved in a mixture of water (10 ml) and conc. HCl (2.0 ml). The temperature was lowered to 0°C and $NaNO_2$ (0.5 g, 7.2 mmol) in H_2O (4 ml) was added dropwise with stirring. After stirring for 1 h, the tetrazonium salt solution was poured into a cold (0°C) solution of Na_2CO_3 (1 g) in H_2O (20 ml), and the resultant solution was poured immediately into a stirred solution of coupling component (7.2 mmol), $NaCO_3$ (3.84 g), $NaHCO_3$ (2.6 g) in H_2O (100 ml). After stirring the reaction mixture for 1 h at 0–5°C, crude dye was precipitated by the addition of NaCl. The dye was collected by filtration, dissolved in H_2O (50 ml), and the solution was acidified using conc. HCl. The precipitated dye was collected by filtration, and purified by dissolution in water and re-precipitation by the addition of KOAc. The dye was collected by filtration and washed with EtOH. The procedure

was repeated twice and the purity of the dye was confirmed by paper chromatography, which showed one component using BuOH/pyridine/H_2O (5:3:5) as the eluent.

2.6. Dye application

A 3% dyeing (owf) was carried out under neutral conditions at a 30:1 liquor ratio. The dyebath temperature was raised to 60°C, and a sample of cotton fabric that had been wet out in hot water was added. The temperature was increased slowly to 95°C and dyeing was continued at this temperature for 30 min and for a further 30 min after adding 10% NaCl (owf). The fabric was removed, rinsed in cold water and air-dried. The fabric was then after-treated with fixing agent levogen BF (2 g/l) at a 20:1 liquor ratio, 50–60°C and pH 4–5 (10% HOAc). Following a 30-min treatment, the fabric was rinsed in cold water and air-dried.

2.7. Wash fastness determination

The dyed fabrics were evaluated using a standard procedure [10]. The method employed 5 g/l soap and was carried out at 50±2°C for 45 min at a 50:1 liquor ratio. The resultant fabric was evaluated for color change and staining of adjacent undyed fabrics. The rating scale was 1 (poor) to 5 (excellent).

2.8. Light fastness determination

The dyed fabrics were evaluated using the standard method GB8427-87 (China), which employs the following conditions:
Operating instrument: XENOTEST 150s (Heraens)
Wavelength range: 300–800 nm.
Stage 1: 1030 W/m^2
Maximum black panel temperature: 45°C (ISO 150-B02)
Humidity: 60%

2.9. Mutagenicity testing

The assays employed were based upon those developed by Ames and co-workers [11]. For this assay, the induced rat liver used in the S9 mix was prepared using male Sprague–Dawley rats. Five strains of *Salmonella typhimurium* were used: TA98, TA100, TA1535, TA1537, and TA1538. In this method, a compound was judged to be mutagenic if the number of revertant colonies was twice the background count (i.e. number of colonies at the 0-μg dose).

3. Results and discussion

3.1. Synthesis

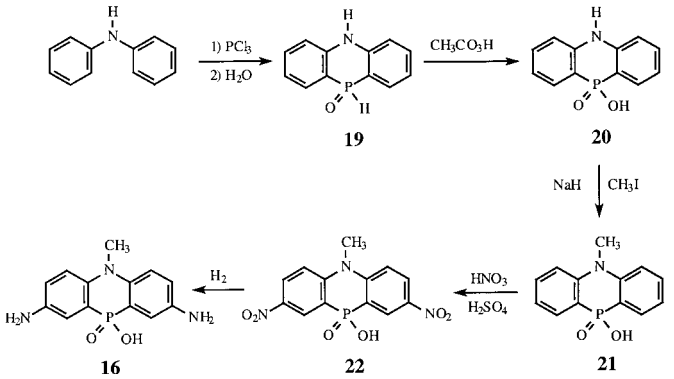
Diamine **16** was synthesized according to the route shown in Scheme 1. Diphenylamine was heated with PCl_3 at 210–220°C followed by hydrolysis of the intermediate chlorophosphine with water, to give compound **19** [12,13]. Treatment of the phosphine oxide with peracetic acid gave **20** in 37% overall yield. Alkylation with CH_3I, nitration using mixed acid, and hydrogenation over 5% Pd/C gave the target diamine. The product was best kept as the dihydrochloride.

Tetrazotisation of **16** was carried out using $NaNO_2$/HCl and coupling under alkaline conditions and acid work up gave good yields of the desired dyes (Scheme 2). In this scheme, H acid, chromotropic acid, J acid, gamma acid and Nevile–Winther's acid were coupled twice to the tetrazonium compound to produce disazo dyes **23–27**, respectively. These dyes include analogues of **3**, **9** and **10**.

Table 1
Spectral data for dyes prepared in this study

Dye	Color	λ_{max} (nm)[a]	E_{max} (l/mol cm^{-1})
23	Blue	611.2	5.5×10^4
24	Blue	615.2	5.0×10^4
25	Reddish blue	570.2	3.5×10^4
26	Navy blue	590.2	3.9×10^4
27	Purple	545.0	3.5×10^4
8	Blue	587.0	4.0×10^4
9	Violet	548.0	4.1×10^4

[a] In H_2O.



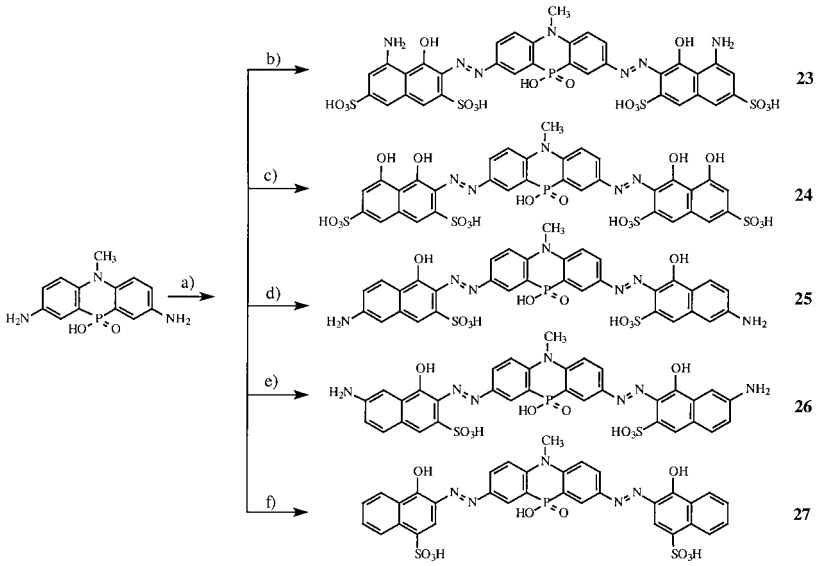
Scheme 1. Six-step synthesis of diamine **16**.

3.2. Spectral data and dyeing properties

The visible absorption spectra of all dyes were recorded in distilled water, the results of which are summarized in Table 1. Coupling of **16** to H acid and chromotropic acid gave dyes with deep blue colors in solution. Replacement of the H acid moiety with J acid gave a reddish blue dye **25**, and using the isomeric gamma acid moiety in lieu of J acid gave a 20 nm bathochromic shift (cf. **26**). Replacement of the J-acid moiety by Nevile–Winther's acid gave a 25 nm hypsochromic shift (cf. **27**).

We also found that **16** could be used to give colors and intensities comparable to those obtained when benzidine was used. Examples are dyes **26** and **27**, which gave λ_{max} and ϵ_{max} values that were quite similar to those recorded for dyes **8** and **9**, respectively.

As anticipated from their spectral properties, dyes **23**, **24** and **26** gave blue shades on cotton, while shades from dyes **25** and **27** were hypsochromic, conferring reddish-blue and purple shades on cotton, respectively. The reddish blue shade obtained with **25** and the navy blue shade obtained with **26**



Scheme 2. Synthesis of dyes used in this investigation. (a) $HCl/NaNO_2$; (b) H acid, pH 9–10; (c) chromotropic acid, pH 9–10; (d) J acid, pH 9–10; (e) gamma acid, pH 9–10; (f) Nevile–Winther's acid, pH 9–10.

Table 2
ESI MS data for dyes prepared in this study

Dye	M/2 ions	M/3 ions	M/4 ions
23	488.8 (4Na)	318 (4Na)	232.9 (4Na)
	477.4 (3Na + H)	310.7 (3Na + H)	249.9 (Na-3H)
	466.6 (2Na + 2H)		
24	489.2 (4Na)	319.1 (4Na)	–
	478.5 (3Na + H)	311.2 (3Na + H)	
	467.5 (2Na + 2H)		
25	386.7 (2Na)	–	–
26	386.5 (2Na)	257.6 (2Na-H)	–
	397.5 (M-H-Na)		
27	371.5 (2Na)	247.4 (2Na)	–
		(2Na-H)	

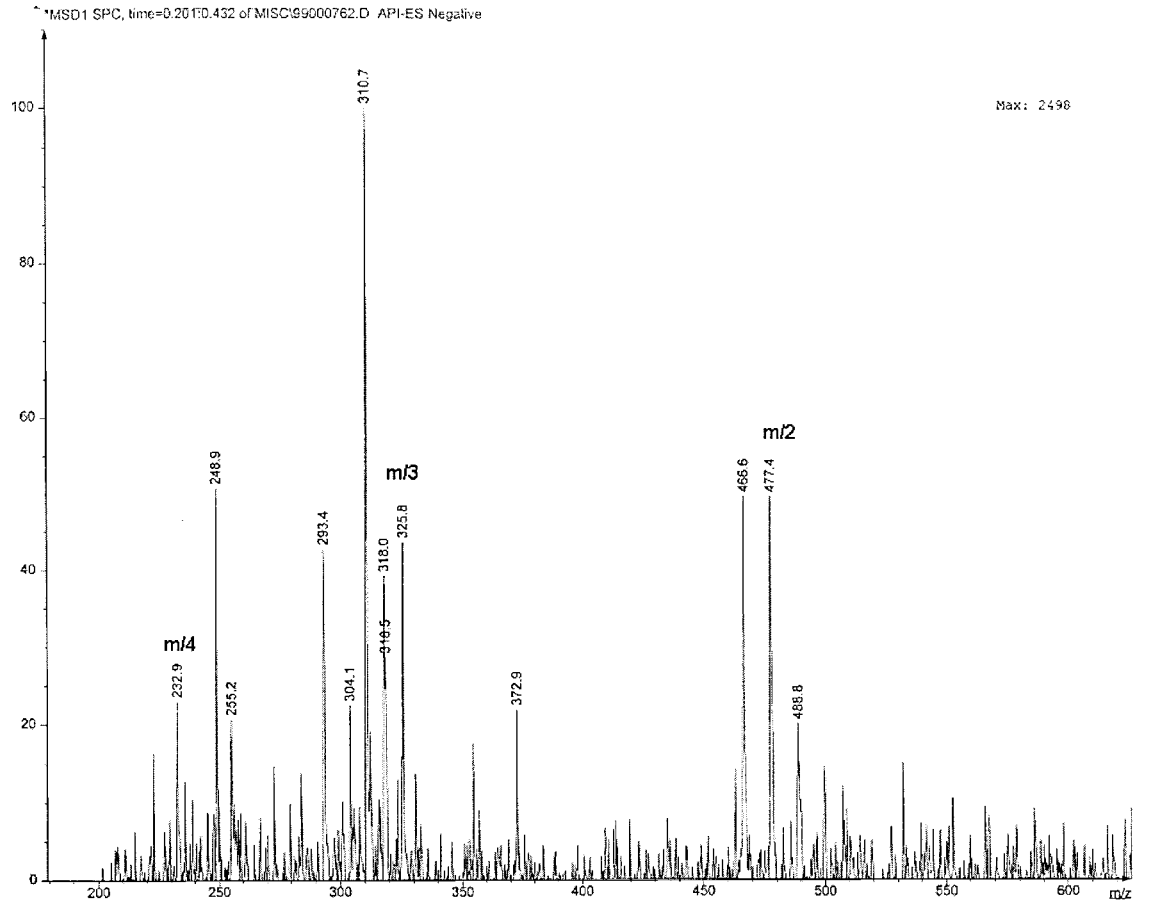


Fig. 1. ESI mass spectrum of dye **23**.

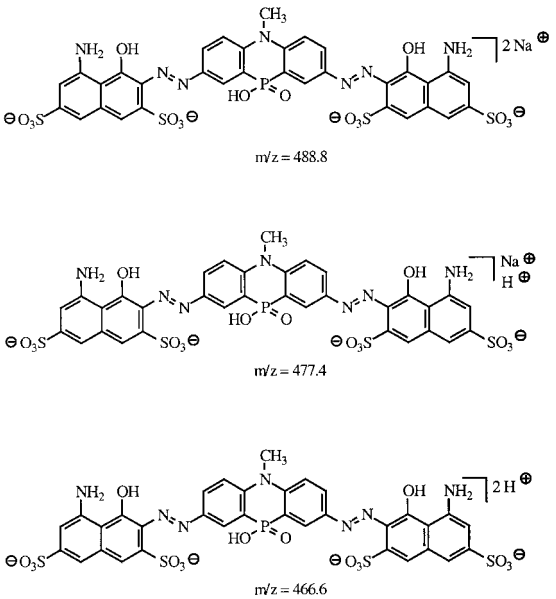


Fig. 2. M/2 species observed in the ESI mass spectrum of dye **23**.

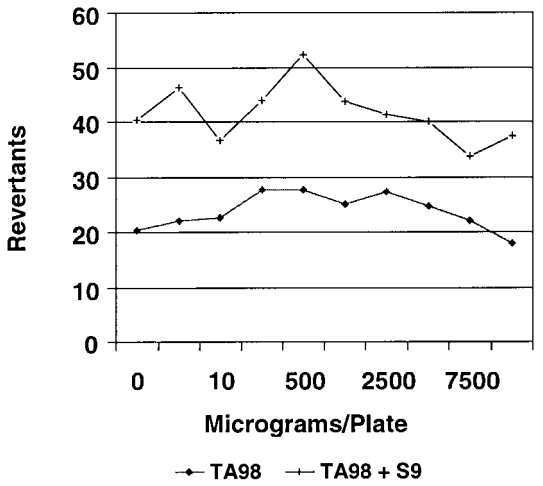


Fig. 3. Mutagenicity data for diamine **16** in TA98 with (lower) and without (upper) S9.

Table 3
Fastness data for dyes prepared in this study

Dye	Light fastness	Wash fastness		
		Change in shade	Staining on cotton	Staining on wool
23	3	3	4	5
24	3–4	3–4	4–5	5
25	2–3	4	2–3	5
26	3	4	2–3	5
27	2	3–4	3	5
8	2–3	4	3	5
9	2	3–4	2–3	5

indicate that the small structural difference between J acid and gamma acid led to significantly different hues following couplings with diamine **16**, as seen with traditional diazo compounds.

3.3. Mass spectrometry

Table 2 contains a summary of the electrospray ionization mass spectrometry (ESI MS) data produced on dyes **23–27**, and Fig. 1 shows a representative spectrum. Data presented correspond to the major analyte signals observed for m/2, m/3, and m/4 species. As expected, dyes **23** and **24** gave the largest number of ions, with signals arising from 2^-, 3^-, and 4^- charges. In some cases, multiple signals having the same charge were observed. For instance, dye **23** gave three m/2 signals, which correspond to the structures shown in Fig. 2. In some cases, signals arising from the ionization of the phosphinic acid moiety were observed. An example is the m/3 signal for dye **26** ($m/z = 257.6$), which corresponds to the (M-2Na-H)/3 species.

3.4. Fastness properties

The results of fastness studies for the new dyes and related commercial dyes are summarized in Table 3. It can be seen from the data that the wash fastness properties of the dyes are good, with a rating of 3–4 for color change, in most cases. Dyes **25** and **26** gave unsatisfactory results in the staining of cotton aspect of the test, which was consistent with the prototypes. There was no staining of wool fabric, however.

The lightfastness was acceptable when **23**, **24** and **26** were employed, each dye giving better lightfastness than the commercial dyes. The best

dye, overall, was **24**, which gave little staining on cotton as well as good lightfastness.

3.5. *Mutagenicity*

Fig. 3 shows data from the evaluation of diamine **16** in the standard *Salmonella*/mammalian microsome assay, with and without metabolic activation (S9). While the specific data shown arise from the use of TA 98, a frame-shift sensitive strain, comparable results were observed using TA100, TA1535, TA1537 and TA1538. All clearly established the diamine as nonmutagenic with and without S9 activation.

4. Conclusion

It has been shown that 2,8-diamino-5,10-dihydro-10-hydroxy-5-methylphenophosphazine 10-oxide (**16**) is a potential replacement for the benzidine moiety of certain known genotoxic azo dyes. This diamine undergoes tetrazotization readily, and generates essentially the same hues exhibited by the benzidine-based dyes containing readily available coupling components. The resultant dyeings also possess satisfactory wash fastness properties. It remains to be established, however, whether the dyes produced are less genotoxic than the corresponding benzidine-based dyes. Those studies are under way.

Acknowledgements

One of the authors, K.A. Bello, acknowledges support from the Dalian Government through a one year fellowship award from the Dalian University of Technology, State Key Laboratory of Dyes and Surfactants, and Department of Fine Chemicals, China.

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