Dyes and Pigments 80 (2009) 245–253

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Potential alternatives for 3,3′-dichlorobenzidine as tetrazo components for diarylide yellow and orange pigments, Part 1: *p*-Phenylenediamine and its derivatives

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ARTICLE INFO

Article history:
Received 18 February 2008
Received in revised form 10 July 2008
Accepted 12 July 2008
Available online 19 July 2008

Keywords:
Disazo pigments
3,3′-Dichlorobenzidine
p-Phenylenediamine
Phenylenediaminedisulphonic acid
Metal salt
Disazoacetoacetanilide

ABSTRACT

A series of diarylide yellow pigments based on selected *p*-phenylenediamine derivatives as tetrazo components have been synthesised and their application performance assessed. Among the most interesting products were a range of new metal-salt disazo pigments synthesised from 2,5-phenylenediamine-1,6-disulphonic acid, which is of potential interest as an alternative to 3,3-dichlorobenzidine, as it is likely to be of low toxicity, non-carcinogenic, non-mutagenic and potentially low cost. The synthesis of disazo metal-salt pigments is in this case complicated by the requirement for a two-stage diazotisation/azo coupling process, although this offers a versatility advantage with an easy route to unsymmetrical derivatives. The colouristic properties, overpaint fastness, lightfastness and heat stability of the metal-salt pigments were comparable in some cases, inferior in others, to commercial dichlorobenzidine-based pigments selected as standards. Lightfastness was, in some cases, comparable in full strength although inferior in tint; solvent resistance was superior to that of the commercial pigments, as expected for metal-salt type pigments.

1. Introduction

The most important group of classical yellow organic pigments are the disazoacetoacetanilides (diarylide yellows) and the most important oranges are disazopyrazolones (diarylide oranges) [1–4]. Most of these pigments, important examples of which include C.I. Pigments Yellow 12 (**1a**), 13 (**1b**) and 83 (**1c**) (Fig. 1), and C.I. Pigments Orange 13 (**2a**) and 34 (**2b**) (Fig. 2), are manufactured from 3,3′-dichlorobenzidine (DCB) (**3**) (Fig. 3) as the tetrazo component, with acetoacetanilides **4a**–**4c** (Fig. 4) and pyrazolones **5a** and **5b** (Fig. 5) as the coupling components used for pigments **1a**–**1c**, **2a** and **2b**, respectively. There are ongoing concerns over the toxicity, in particular the possible mutagenicity, of DCB [5]. However, this diamine remains acceptable as an intermediate for use in industrial pigment manufacture worldwide provided that stringent handling precautions are adopted in the workplace. There is no convincing evidence that the diarylide yellow and orange pigments themselves present any significant toxicological hazard. However, it has been reported that thermal treatment of polymers containing diarylide yellow pigments above 200 °C, and particularly prolonged treatment in the higher temperature range of 240–300 °C, can cause thermal cleavage of the pigments, leading to the release of aromatic amines, including DCB, so that there is some concern over their use in applications where they may be subjected to high temperatures, such as in thermoplastics [6]. Consequently, there remains interest in alternative diarylide pigments involving the use of potentially safer intermediates.

Previously, some diarylide yellow pigments based on specifically designed non-mutagenic benzidine derivatives have been reported [7,8]. In the investigations described in this paper and subsequent publications, a different approach is adopted in which a range of disazo pigments structurally analogous to the commercial diarylide pigments have been synthesised with diamines, selected on the basis of decreased likelihood of genotoxicity and potential low cost. In this paper, we report the synthesis of disazo pigments based on derivatives of 1,4-phenylenediamine, together with a technical evaluation in an industrial paint formulation.

2. Experimental

2.1. Instrumental methods

FTIR spectra were recorded as KBr discs with a Nicolet Protégé 460 Fourier Transform Infra-red spectrophotometer and OMNIC software. Melting points and decomposition temperatures were determined using a Mettler 12E Differential Scanning Calorimeter (DSC).

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doi:10.1016/j.dyepig.2008.07.006

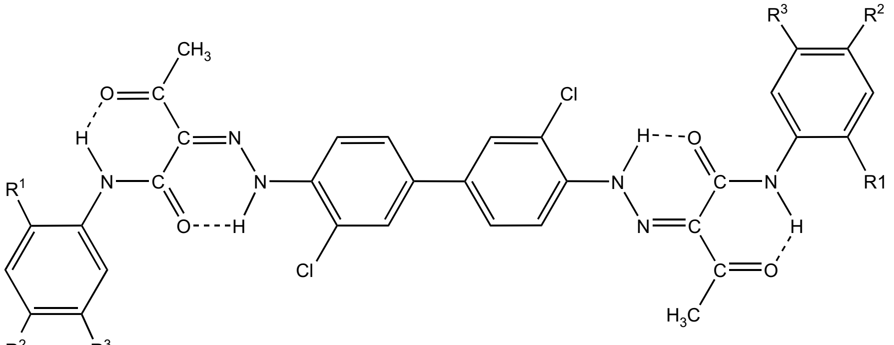

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Fig. 1. Structures of diarylide yellow pigments; **1a**: $R^1 = R^2 = R^3 = H$; **1b**: $R^1 = R^2 = CH_3$, $R^3 = H$; **1c**: $R^1 = R^3 = OCH_3$, $R^2 = Cl$.

UV/vis spectra were measured on a Perkin–Elmer Lambda 2 spectrophotometer as solutions in dimethylformamide (DMF). ^1H NMR spectra were obtained with a Bruker AC 200 (^1H at 200 MHz). C, H, N analysis utilised the Exeter CE-440 Elemental Analyser. Colour measurement used a Datacolor International Spectraflash SF600 spectrophotometer with Datacolor International Management System software.

2.2. Standard pigments

As standards, the commercial pigments used were *Irgalite Yellow BO* (**1a**, C.I. Pigment Yellow 12), *Irgalite Yellow BAW* (**1b**, C.I. Pigment Yellow 13), *Irgalite Orange P* (**2a**, C.I. Pigment Orange 13), *Irgalite Orange F2G* (**2b**, C.I. Pigment Orange 34) (all Ciba Specialty Chemicals), and *Hostaperm Yellow HR* (**1c**, C.I. Pigment Yellow 83) (Clariant). Resins *BA 595* and *BE 672* were supplied by Ciba Specialty Chemicals, UK.

2.3. Synthesis

2.3.1. Preparation of pigments ***7a*–*7d*** and ***8a*–*8c***, based on 1,4-phenylenediamine and derivatives [9]

1,4-Phenylenediamine (**6a**) (2.25 g, 0.025 mol) or 2,5-dichloro-1,4-phenylenediamine (**6b**) (4.43 g, 0.025 mol) was ground in a mortar and pestle, added to concentrated phosphoric acid (50 cm^3) and the solution cooled to −5 °C in an ice/salt bath. Sodium nitrite (3.8 g, 0.055 mol) was added very slowly to concentrated sulphuric acid (30 cm^3) in a cold water bath. Once complete, the resulting mixture was heated to 60 °C until all the nitrite were dissolved and then cooled down in an ice/salt bath. Nitrosylsulphuric acid solution obtained was slowly added to the acidic amine solution whilst the temperature was maintained at −5 °C for 1,4-phenylenediamine (**6a**), but for 2,5-dichloro-1,4-phenylenediamine (**6b**) the temperature was maintained at approximately −25 °C with the addition of dry ice. The solutions were stirred for 2 h and excess nitrous acid destroyed by the addition of sulphamic acid.

Acetoacetanilide (**4**) or pyrazolone (**5**) coupling component (0.055 mol) was dissolved in a solution of sodium hydroxide (11.0 g) in water (250 cm^3). When completely dissolved, anhydrous sodium acetate (50 g) was added with continuous stirring until a clear solution was obtained. A mixture of glacial acetic acid and water (1:5) was added dropwise until the coupling component reprecipitated, and the pH reached 7.0. The tetrazotised diamine solution was added dropwise to the coupling component keeping the pH in the range 6.5–7.0 with the simultaneous addition of aqueous 2 M sodium hydroxide solution. Excess tetrazo component was avoided throughout (H-acid test). After coupling was complete the pigment suspension was heated, with stirring, to 90–95 °C for 1.5 h, filtered hot and washed salt-free. The pigment was then dried at 90 °C.

Compound **7a** was isolated as a yellow powder (81%) from *N*-phenyl-3-oxobutanamide (**4a**) (acetoacetanilide). m.p. 288 °C, decomp. 333 °C; ν_{max}/cm^{-1}: 1661 (C=O str), 1596, 1556, 1247. Compound **7b** was isolated as a yellow powder (77%) from *N*-(2′,4′-dimethylphenyl)-3-oxobutanamide (AAMX) (**4b**). m.p. 297 °C, decomp. 324 °C; ν_{max}/cm^{-1}: 1660 (C=O str), 1595, 1552, 1261. Compound **7c** was obtained as a yellow powder (76%) from *N*-(4′-chloro-2′,5′-dimethoxyphenyl)-3-oxobutanamide (AADMCA) (**4c**). m.p. 349 °C, decomp. 355 °C; ν_{max}/cm^{-1}: 1659 (C=O str), 1591, 1269. Compound **7d** was obtained as a brownish yellow powder (52%) from *N*-phenyl-3-oxobutanamide (acetoacetanilide) (**4a**). m.p. 313 °C, decomp. 360 °C; ν_{max}/cm^{-1}: 1669 (C=O str), 1596, 1246 cm^{-1}. Compound **8a** was obtained as an orange powder (73%) from 3-methyl-1-phenylpyrazolone (**5a**). decomp. 300 °C; ν_{max}/cm^{-1}: 1660 (C=O str), 1548, 1488, 1253. Compound **8b** was obtained as an orange powder (88%) from 3-methyl-1-(4′-methylphenyl)pyrazolone (**5b**). decomp. 329 °C; ν_{max}/cm^{-1}: 1655 (C=O

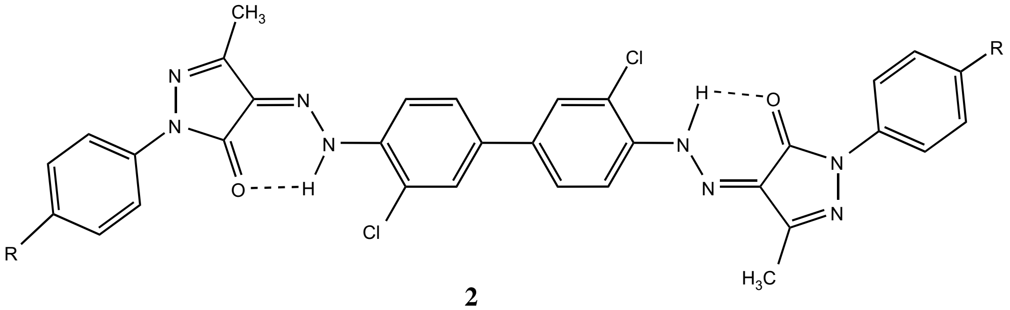

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Fig. 2. Structures of diarylide orange pigments; **2a**: R = H; **2b**: $R = CH_3$.

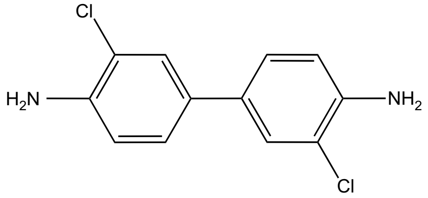

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Fig. 3. 3,3′-Dichlorobenzidine (DCB).

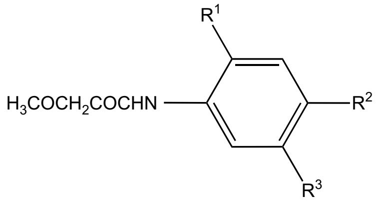

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Fig. 4. Acetoacetanilide coupling components; **4a**: $R^1 = R^2 = R^3 = H$; **4b**: $R^1 = R^2 = CH_3$, $R^3 = H$; **4c**: $R^1 = R^3 = OCH_3$, $R^3 = Cl$.

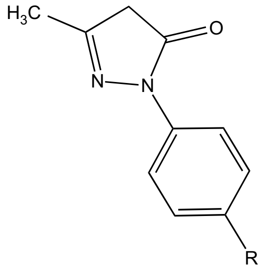

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Fig. 5. Pyrazolone coupling components; **5a**: R = H; **5b**: $R = CH_3$.

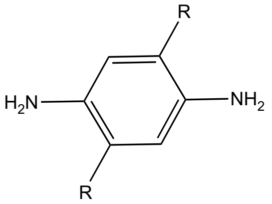

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Fig. 6. *p*-Phenylenediamine derivatives; **6a**: R = H; **6b**: R = Cl; **6c**: $R = SO_3H$.

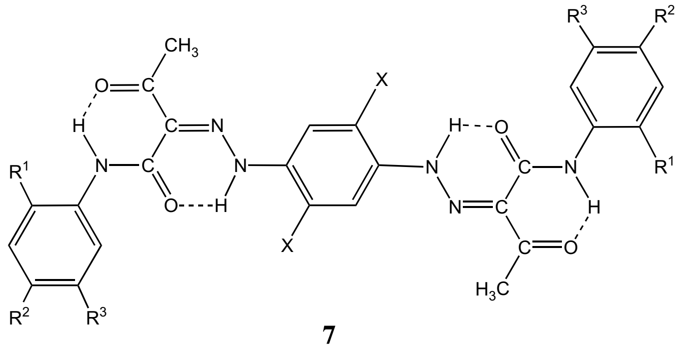

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Fig. 7. Diarylide yellow pigments based on *p*-phenylenediamines; **7a**: $R^1 = R^2 = R^3 = H$, X = H; **7b**: $R^1 = R^2 = CH_3$, $R^3 = H$, X = H; **7c**: $R^1 = R^3 = OCH_3$, $R^3 = Cl$, X = H; **7d**: $R^1 = R^2 = R^3 = H$, X = Cl.

str), 1546, 1509, 1245. Compound **8c** was obtained as a brown-red powder (61%) from 3-methyl-1-phenylpyrazolone (**5a**). m.p. 227 °C, decomp. 350 °C; ν_{max}/cm^{-1}: 1666 (C=O str), 1548, 1500, 1233.

*2.3.2. Synthesis of pigments **12a–12d** and **13** from 2,5-phenylenediamine-1,6-disulphonic acid (**6c**) [10]*

*2.3.2.1. Diazotisation of 2,5-phenylenediamine-1,6-disulphonic acid (**6c**)[11].* 2,5-Phenylenediamine-1,6-disulphonic acid (**6c**) (30.18 g, 0.1125 mol) was added with stirring to a mixture of water (180 cm^3) and concentrated hydrochloric acid (36 cm^3). The fine suspension was cooled to −5 °C in an ice/salt bath, and 5 M aqueous sodium nitrite (23 cm^3, 0.1150 mol) was added dropwise so that the temperature did not exceed 5 °C. This was stirred for 1 h to give a brown suspension which was used immediately. Excess nitrite was destroyed with sulphamic acid using starch/iodide paper as an indicator.

*2.3.2.2. Procedure for first coupling reaction to give monoazo derivatives' disodium salts **10** and **11**.* The coupling component (0.1130 mol) was dissolved in a solution of sodium hydroxide (22.50 g) in water (200 cm^3). Once the solid had completely dissolved, anhydrous sodium acetate (90 g) was added with continuous stirring until a clear solution was obtained. A mixture of glacial acetic acid and water (1:5) was added dropwise until the coupling component reprecipitated, and the pH reached 7.0. The diazonium salt was added dropwise to the coupling component suspension keeping the pH in the range 7–8 with the simultaneous addition of 5 M sodium hydroxide solution. Excess diazonium salt was avoided throughout (H-acid test). After coupling was complete (60–90 min) the dispersion was heated, with stirring, to 90–95 °C for 45 min, then cooled to 5 °C to allow complete precipitation out of solution. The monoazo disodium salt was filtered and dried in vacuum oven at 65 °C.

Compound **10a** was obtained as a yellow powder from **4a**; decomp. 394 °C; δ_H (200 MHz, DMSO-d_6): 2.48 (s, 3H, CH_3CO), 5.80 (br s, 2H, NH_2), 7.03 (s, 1H, H_a), 7.06–7.15 (m, 1H, H_e), 7.31–7.40 (m, 2H, $H_{d,f}$), 7.62–7.68 (m, 2H, $H_{c,g}$), 7.92 (s, 1H, H_b), 11.36 (br s, 1H, amide NH), 14.70 (br s, 1H, hydrazone NH); ν_{max} (KBr)/cm^{-1}: 3361 (N–H str), 1673 (C=O str), 1564, 1514. Compound **10b** was obtained as a yellow powder from **4b**; decomp. 388 °C; δ_H (200 MHz, DMSO-d_6): 2.15 (s, 3H, *p*-CH_3), 2.23 (s, 3H, *o*-CH_3), 2.48 (s, 3H, CH_3CO), 5.80 (br s, 2H, NH_2), 6.90–7.09 (m, 2H, $H_{d,f}$), 7.03 (s, 1H, H_a), 7.93 (s, 1H, H_b), 8.07 (d, 1H, H_g), 11.27 (br s, 1H, amide NH), 14.81 (br s, 1H, hydrazone NH); ν_{max} (KBr)/cm^{-1}: 3278 (N–H str), 1664 (C=O str), 1601 (aromatic C=C str). Compound **10c** was obtained as a yellow/orange powder from **4c**; decomp. 391 °C. δ_H (200 MHz, DMSO-d_6): 2.46 (s, 3H, CH_3CO), 3.81 (s, 3H, *o*-OCH_3), 3.88 (s, 3H, *p*-OCH_3), 5.81 (br s, 2H, NH_2), 7.03 (s, 1H, H_a), 7.17 (s, 1H, H_d), 7.91 (s, 1H, H_b), 8.28 (s, 1H, H_g), 11.79 (br s, 1H, amide NH), 14.73 (br s, 1H, hydrazone NH); ν_{max} (KBr)/cm^{-1}: 3461 (N–H str), 1654 (C=O str), 1537, 1505. Compound **11a** was isolated as a red powder from **5a**. No m.p. or decomp. < 400 °C. δ_H (200 MHz, DMSO-d_6): 5.95 (br s, 2H, NH_2), 7.05 (s, 1H, H_a), 7.12–7.21 (m, 1H, H_e), 7.37–7.47 (m, 2H, $H_{f,d}$), 7.89–8.02 (m, 3H, $H_{b,c,g}$), 14.17 (br s, 1H, hydrazone NH); ν_{max} (KBr)/cm^{-1}: 3340 (N–H str), 1663 (C=O str), 1542, 1504. Compound **11b** was isolated as a red powder from **5b**. No m.p. or decomp. < 400 °C. δ_H (200 MHz, DMSO-d_6): 2.28 (s, 3H, *p*-CH_3), 2.30 (s, 3H, pyrazolone CH_3), 5.90 (br s, 2H, NH_2), 7.05 (s, 1H, H_a), 7.16–7.26 (m, 2H, $H_{f,d}$), 7.81–7.92 (m, 3H, $H_{b,c,g}$), 14.15 (br s, 1H, hydrazone NH); ν_{max} (KBr)/cm^{-1}: 3408 (N–H str), 1659 (C=O str).

*2.3.2.3. Preparation of disodium salts of disazo compounds **12(I)** and **13(I)**.* The monoazo derivatives were obtained from the procedure mentioned in Section 2.3.2.2 reasonably, but not rigorously, salt-free. Percentage yields quoted for the disazo products are thus subject to the inherent approximation in the assumed molar quantities of monoazo derivatives.

The monoazo compound (approx. 0.065 mol) was added to a mixture of water (60 cm^3) and concentrated hydrochloric acid (22 cm^3). The mixture was then cooled in an ice/salt bath to −5 °C. Aqueous sodium nitrite, 5 M (13.5 cm^3, 0.0675 mol), was added very slowly so that the temperature did not exceed 0 °C. This was stirred for 1 h to give a brown suspension which was used immediately. Excess nitrite was destroyed, prior to coupling, with dilute aqueous sulphamic acid using starch/iodide paper as an indicator.

The coupling component (0.067 mol) was dissolved in a solution of sodium hydroxide (14.47 g) in water (175 cm^3). Anhydrous sodium acetate (65.80 g) was then added with continuous stirring until dissolved. A mixture of glacial acetic acid and water (1:5) was added dropwise until the coupling component reprecipitated, and the pH reached 7.0. The diazo component was added dropwise to the coupling component keeping the pH in the range 6.5–7.0 with simultaneous addition of 5 M sodium hydroxide solution. Excess diazo component was avoided throughout (H-acid test). After coupling was complete (approx. 60–90 min) the dispersion was heated, with stirring, to 90–95 °C for 1 h and then cooled to room temperature. The suspension was then filtered, washed, and dried in the vacuum oven at 65 °C. Analytical samples, where appropriate, were obtained by recrystallisation from minimum volumes of water.

Compound **12a**(**I**) was obtained as yellow powder (80%) from **10a** as diazo component and **4a** as coupling component; decomp. 397 °C. δ_H (200 MHz, DMSO-d_6): 2.53 (s, 6H, CH_3CO), 7.09–7.19 (m, 2H, H_d), 7.33–7.43 (m, 4H, $H_{c,e}$), 7.65–7.75 (m, 4H, $H_{b,f}$), 8.15 (s, 2H, H_a), 11.13 (br s, 1H, amide NH), 14.43 (br s, 2H, hydrazone NH); ν_{max}/cm^{-1}: 3524 (N–H str), 1671 (C=O str), 1560, 1511. Elemental analysis: found: C, 44.9; H, 3.3; N, 11.7. $C_{26}H_{22}N_6O_{10}S_2Na_2 \cdot 0.5H_2O$ requires C, 44.8; H, 3.2; N, 12.0%. Compound **12b**(**I**) was obtained as an orange/brown powder (90%) from **10a** as diazo component and **4b** as coupling component. No m.p. or decomp. < 400 °C. δ_H (200 MHz, DMSO-d_6): 2.26 (s, 3H, *p*-CH_3), 2.30 (s, 3H, *o*-CH_3), 2.55 (s, 6H, 2 × CH_3CO), 6.98–7.19 (m, 3H, H_{d,c^*,e^*}), 7.31–7.43 (m, 2H, $H_{c,e}$), 7.65–7.75 (m, 2H, $H_{b,f}$), 8.01–8.08 (m, 1H, H_{f^*}), 8.17 (s, 2H, H_{a,a^*}), 11.13 (br s, 2H, amide NH), 14.42 and 14.74 (s, 1H + 1H, hydrazone H); ν_{max}/cm^{-1}: 3449 (N–H str), 1665 (C=O str), 1560, 1490. Elemental analysis: found: C, 46.0; H, 3.8; N, 11.7. $C_{28}H_{26}N_6O_{10}S_2Na_2 \cdot H_2O$ requires C, 45.8; H, 3.8; N, 11.4%. Compound **12c**(**I**) was isolated as an orange/brown powder (70%) from **10a** as diazo component and **4c** as coupling component. decomp. 341 °C. δ_H (200 MHz, DMSO-d_6): 2.54 (s, 6H, 2 × CH_3CO), 3.83 (s, 3H, *o*-OCH_3), 3.90 (s, 3H, *p*-OCH_3), 7.09–7.21 (m, 3H, H_{d,c^*,f^*}), 7.32–7.44 (m, 2H, $H_{c,e}$), 7.63–7.72 (m, 2H, $H_{b,f}$), 8.17 (s, 2H, H_{a,a^*}), 11.12 and 11.68 (br s, 1H + 1H, amide NH), 14.41 and 14.72 (br s, 1H + 1H, hydrazone NH); ν_{max}/cm^{-1}: 3435 (N–H str), 1665 (C=O str), 1494, 1212. Elemental analysis: found: C, 42.0; H, 3.3; N, 10.4. $C_{28}H_{26}N_6ClO_{12}S_2Na_2 \cdot H_2O$ requires C, 41.9; H, 3.5; N, 10.5%. Compound **12d**(**I**) was obtained as a yellow/orange powder (83%) from **10b** as diazo component and **4b** as coupling component. No m.p. or decomp. < 400 °C. δ_H (200 MHz, DMSO-d_6): 2.27 (s, 6H, CH_3CO), 2.30 (s, 6H, *o*-CH_3), 2.55 (s, 6H, *p*-CH_3), 6.99–7.11 (m, 4H, $H_{c,e}$), 8.01–8.07 (m, 2H, H_f), 8.18 (s, 2H, H_a), 11.11 (br s, 2H, amide NH), 14.73 (br s, 2H, hydrazone NH); ν_{max}/cm^{-1}: 3408 (N–H str), 1665 (C=O str), 1554, 1519. Elemental analysis: calc. (%) for $C_{30}H_{30}N_6O_{10}S_2Na_2$: C, 48.4; H, 4.1; N, 11.3; found: C, 48.2; H, 4.0; N, 11.0. Compound **13**(**I**) was obtained as a red powder (78%) from **11a** as diazo component and **5a** as coupling component. No m.p. or decomp. < 400 °C. δ_H (200 MHz, DMSO-d_6): 2.34 (s, 6H, CH_3), 7.16–7.26 (m, 2H, H_d), 7.46–7.51 (m, 4H, $H_{c,e}$), 7.91–7.99 (m, 4H, $H_{b,f}$), 8.17 (s, 2H, H_a), 14.14 (br s, 2H, hydrazone H); ν_{max}/cm^{-1}: 3436 (N–H str), 1677 (C=O str), 1543, 1500. Elemental analysis: found: C, 43.6; H, 3.3; N, 15.7. $C_{26}H_{20}N_8O_8S_2Na_2 \cdot 2H_2O$ requires C, 43.5; H, 3.4; N, 15.6%.

*2.3.2.4. Preparation of disazo 1,4-phenylenediamine-2,5-disulphonic acid-based pigments, calcium and manganese salts **12(II)**, **12(III)**, **13(II)** and **13(III)**.* The sodium salt of the disazo 2,5-phenylenediamine-1,6-disulphonic acid derivative (0.015 mol) was added to water (120 cm^3) and heated to boil. Calcium chloride (1.72 g, 0.0155 mol) or manganese(II) chloride tetrahydrate (3.07 g, 0.0155 mol) was added and the mixture was stirred for 1 h at 90–95 °C, filtered hot and washed salt-free (silver nitrate test). The pigment was then dried in the oven at 65 °C.

Compound **12a**(**II**) was obtained as a yellow powder (98%); decomp. 397 °C; ν_{max}/cm^{-1}: 3448 (N–H str), 1668 (C=O str), 1560, 1510. Elemental analysis: found: C, 42.1; H, 3.9; N, 11.1. $C_{26}H_{22}N_6O_{10}S_2Ca \cdot 3H_2O$ requires C, 42.4; H, 3.8; N, 11.4. Compound **12a**(**III**) was obtained as a yellow powder (98%); decomp. 395 °C; ν_{max}/cm^{-1}: 3442 (N–H str), 1670 (C=O str), 1560, 1511. Compound **12b**(**II**) was obtained as an orange/brown powder (75%). No m.p. or decomp. < 400 °C; ν_{max}/cm^{-1}: 3442 (N–H str), 1664 (C=O str), 1558, 1490. Compound **9b**(**III**) was obtained as an orange/brown powder (79%). No m.p. or decomp. < 400 °C; ν_{max}/cm^{-1}: 3422 (N–H str), 1664 (C=O str), 1557, 1489. Compound **12c**(**II**) was isolated as an orange/brown powder (79%); decomp. 355 °C; ν_{max}/cm^{-1}: 3436 (N–H str), 1663 (C=O str), 1490, 1212. Compound **12c**(**III**) was isolated as an orange/brown powder (81%); decomp. 315 °C; ν_{max}/cm^{-1}: 3393 (N–H str), 1662 (C=O str), 1490, 1212.

Compound **12d**(**II**) was obtained as an orange/yellow powder (30%). No m.p. or decomp. < 400 °C; ν_{max}/cm^{-1}: 3448 (N–H str), 1665 (C=O str), 1554, 1518. Compound **12d**(**III**) was obtained as an orange/yellow powder (41%). No m.p. or decomp. < 400 °C; ν_{max}/cm^{-1}: 3449 (N–H str), 1665 (C=O str), 1555, 1519. Compound **13**(**II**) was obtained as a red powder (99%); decomp. 370 °C; ν_{max}/cm^{-1}: 3436 (N–H str), 1657 (C=O str), 1542, 1497. Compound **13**(**III**) was obtained as a red powder (96%); decomp. 371 °C; ν_{max}/cm^{-1}: 3436 (N–H str), 1666 (C=O str), 1543, 1499.

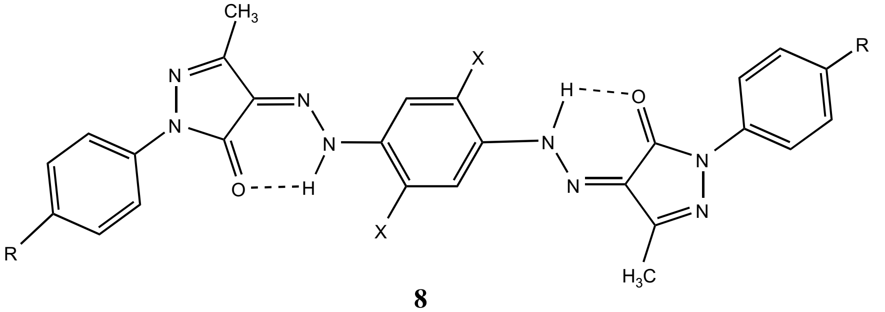

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Fig. 8. Diarylide orange pigments based on *p*-phenylenediamines; **8a**: R = H, X = H; **8b**: R = CH_3, X = H; **8c**: R = H, X = Cl.

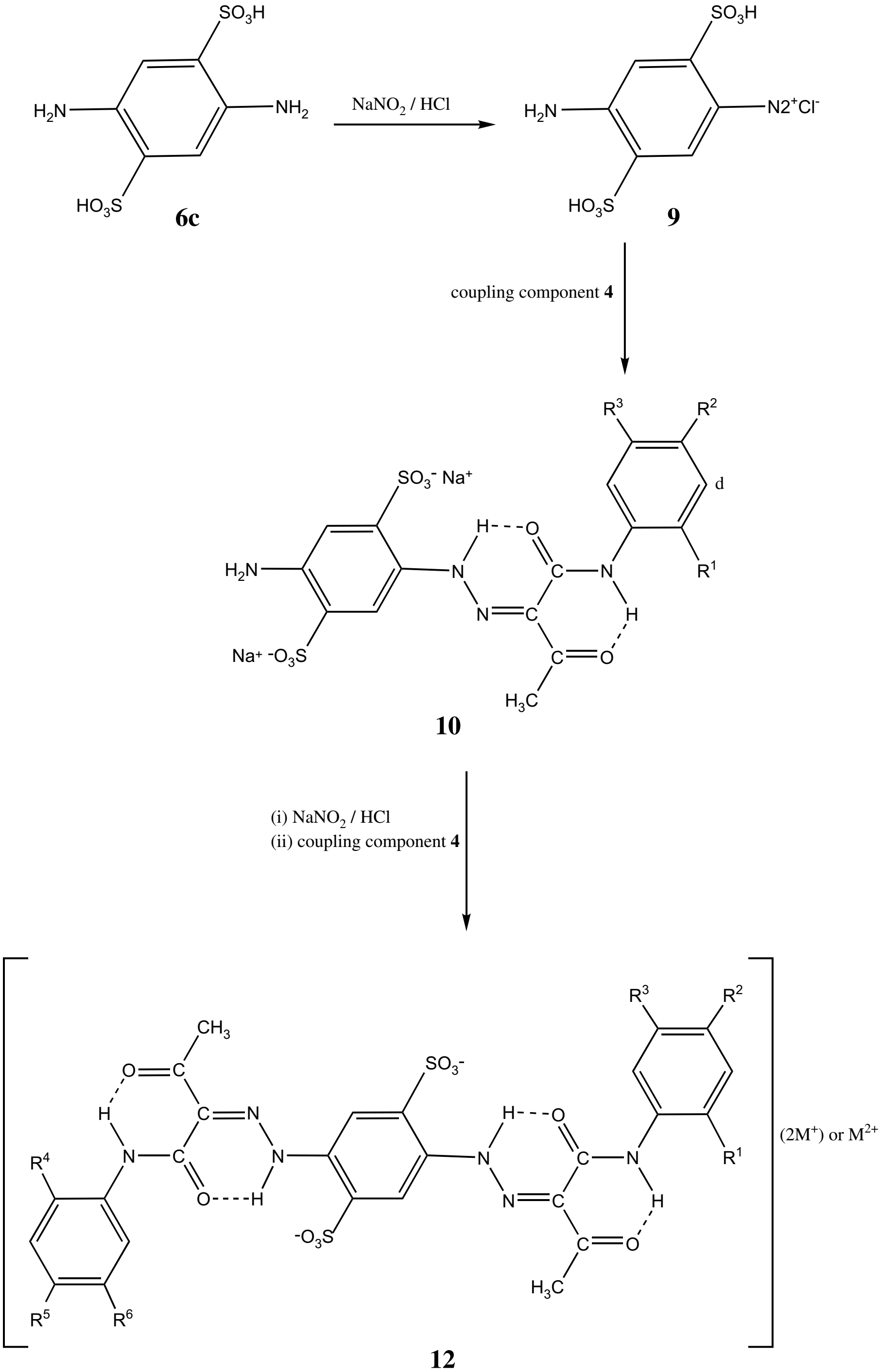
2.4. Application evaluation [12]

2.4.1. Preparation of industrial paints

Pigment (3.75 g), non-drying alkyd resin based on coconut oil BA 595 (10.0 g), and xylene/butan-1-ol (4:1) (25.0 g) were weighed into a 1-lb honey jar. About 10 mm steatite balls (250 g) were then added and the jar was rotated at 120 rpm on rollers for 16 h. A further quantity of BA 595 (32.0 g) was then added and milling continued for 20 min. Isobutylated melamine-formaldehyde resin BE 672 (13.0 g) was then added and the paint preparation completed by milling for a further 10 min. The paint was then obtained by decantation from the steatite balls. A standard white paint was also prepared by a similar process using Tioxide R-CR2 (75.0 g), xylene/butan-1-ol (4:1) (63.0 g), BA 595 resin (30.0 g and then 94.0 g = 124.0 g total) and BE 672 (38.1 g).

2.4.2. Colouristic properties

For the assessment of colouristic properties, drawdowns of the full-strength paint and 1:3 reduction (8.50 g of coloured paint with 4.50 g of white paint) were prepared on Astralux card using a 8-μm K-bar (Sheen Instruments, Kingston-on-Thames, UK). The prepared drawdowns were placed in a fume cupboard for 10 min to allow



Scheme 1. Reaction scheme leading to mono- and disazoacetoacetanilides from **6c**.

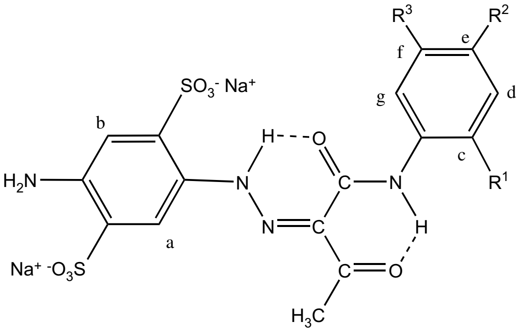


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Fig. 9. Monoazoacetoacetanilides from **6c**, with position identification for NMR interpretation; **10a**: $R^1 = R^2 = R^3 = H$; **10b**: $R^1 = R^2 = CH_3$, $R^3 = H$; **10c**: $R^1 = R^3 = OCH_3$, $R^2 = Cl$.

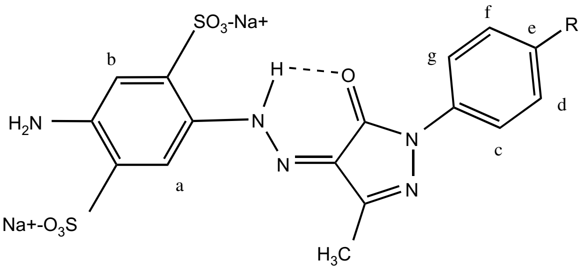

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Fig. 10. Monoazopyrazolones from **6c**, with position identification for NMR interpretation; **11a**: R = H; **11b**: $R = CH_3$.

a certain degree of solvent evaporation, and then stoved at 140 °C for 60 min.

2.4.3. Overpaint fastness

Drawdowns using the pigmented paints were prepared, as described in Section 2.3.2.1 and stoved for 30 min at 140 °C. The drawdown was then partly overpainted with the standard white paint using a 150-μm K-bar (Sheen Instruments, Kingston-on-Thames, UK). The drawdown was then placed in a fume cupboard for 10 min to allow solvent to evaporate and then cured in an oven at 140 °C for 30 min. The 'bleed' was then assessed as ΔE values between the white and overpainted layers.

2.4.4. Lightfastness

Strips of the drawdowns were exposed on a Xenotest 150 Fadometer for 350 h. Lightfastness was assessed by comparison with the Blue Wool Scale and by colour measurement.

2.4.5. Heat stability

A drawdown of the 1:3 reduction was cured in an oven at 140 °C for 15 min. The drawdown was compared by colour measurement with the drawdown cured at 140 °C for 60 min as ΔE values.

3. Results and discussion

3.1. Synthesis and characterisation

This initial investigation has focussed on the simple aromatic diamines, 1,4-phenylenediamine (**6a**), 2,5-dichloro-1,4-phenylenediamine (**6b**), and 2,5-phenylenediamine-1,6-disulphonic acid (**6c**) (Fig. 6). These diamines were chosen on the basis of a combination of structural considerations,

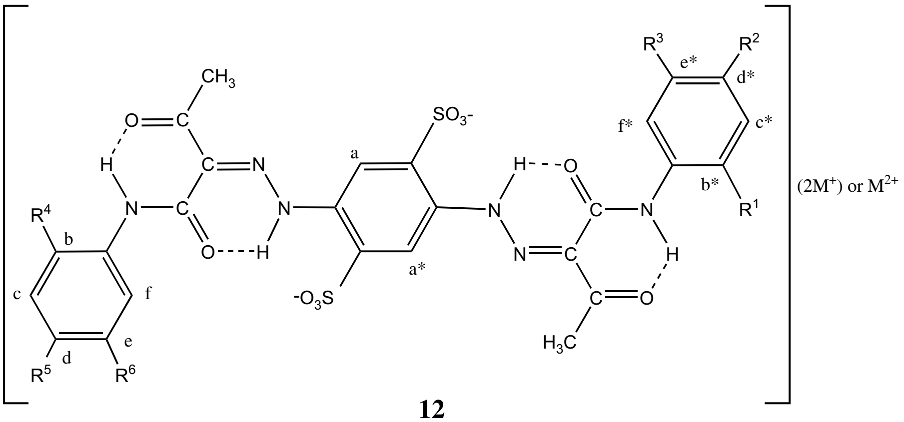

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Fig. 11. Disazoacetoacetanilide metal-salt pigments, with position identification for NMR interpretation: **I** ($M = 2Na^+$), **II** ($M = Ca^{2+}$) and **III** ($M = Mn^{2+}$); **12a**: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$; **12b**: $R^1 = R^2 = CH_3$, $R^3 = R^4 = R^5 = R^6 = H$; **12c**: $R^1 = R^3 = OCH_3$, $R^2 = Cl$, $R^4 = R^5 = R^6 = H$; **12d**: $R^1 = R^2 = R^4 = R^5 = CH_3$, $R^2 = R^5 = H$.

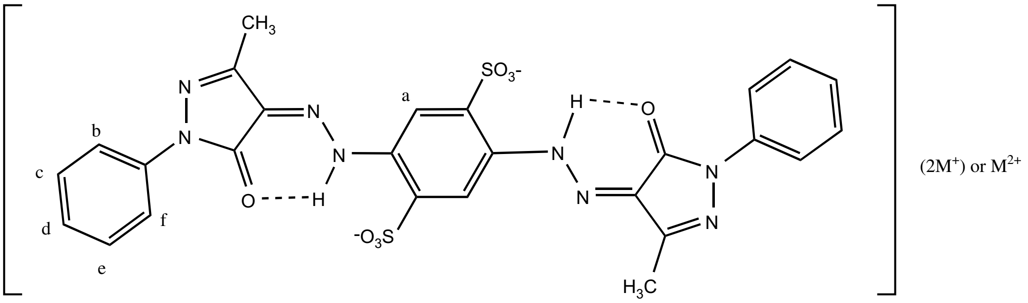

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Fig. 12. Disazopyrazolone metal-salt pigments, with position identification for NMR interpretation: **I** ($M = 2Na^+$), **II** ($M = Ca^{2+}$) and **III** ($M = Mn^{2+}$).

availability, cost, and probable non-mutagenicity. Compound **6a** is used extensively in permanent hair colouration and, although its toxicological profile has been questioned, it remains acceptable for such applications. Compound **6b** was selected to provide more realistic comparability with DCB in view of the presence of the chloro substituents, rather than on the basis of toxicology. Compound **6c** contains sulphonic acid groups. Technically, this allows the formation of metal salts of alkaline earth or transition metals, a feature which is commonly used to give azo pigments with high resistance to solvents. Additionally, the sulphonate group offers the possibility of intramolecular hydrogen bonding to the hydrazone N–H to provide improved lightfastness. Finally, it is well-established that the presence of the sulphonate group provides aromatic amines of low toxicity [13]. Acetoacetanilides **4a**–**4c** (Fig. 4) and pyrazolones **5a** and **5b** (Fig. 5) were used as coupling components to allow direct comparisons with commercial pigments **1a**–**1c**, **2a** and **2b**, respectively.

1,4-Phenylenediamine (**6a**) was tetrazotised in a phosphoric/sulphuric acid mixture using nitrosylsulphuric acid at −5 °C [9]. Yellow pigments **7a**–**7c** (Fig. 7) and orange pigments **8a** and **8b** (Fig. 8) were obtained in good yields (73–88%) by coupling at pH 6.5–7.0. We have previously reported the preparation and rigorous characterisation of **7a** [14]. FTIR spectra of the new pigments **7b**, **7c**, **8a** and **8b** are consistent with their existence in the ketohydrazone form, for example, giving carbonyl stretching frequencies in the range 1659–1669 cm^{-1}, characteristic of these pigment types [14–17]. The tetrazonium salt from **6b** proved to be highly unstable, showing significant evolution of nitrogen gas if the temperature rose above ca −15 °C, and thus required the use of very low temperature tetrazotisation and coupling conditions. Pigments **7d** and **8c** were obtained from this tetrazo component, but in lower yield and as brownish products, presumably due to the unavoidable formation of coloured tetrazonium salt decomposition products, so that pigments of this type were not investigated further.

2,5-Phenylenediamine-1,4-disulphonic acid (**6c**) may be synthesised in good yield and purity by sulphonation of **6a** using oleum [10]. It is thus a potentially inexpensive intermediate. Unlike **6a**, compound **6c** cannot be tetrazotised [11]. However, disazo compounds may be synthesised in a two-stage process. Compound **6c** is easily monodiazotised and the resulting diazonium salt (**9**) undergoes azo coupling to give the monoazo derivatives **10a**–**10c** (illustrated in Scheme 1 for the acetoacetanilides, Fig. 9), **11a** and **11b** (Fig. 10), as their disodium salts. The reactions proceeded smoothly. FTIR spectra of compounds **10a**–**10c**, **11a** and **11b** showed C=O and N–H stretching vibrations, consistent with their existence in the ketohydrazone tautomeric form in the solid state. The ketohydrazone tautomeric form of the disodium salts in solution was confirmed by the assignment of ^{1}H NMR spectra, in comparison with structurally related monoazo pigments [18]. The amino group of intermediates **10a**, **10b** and **11a** was capable of diazotisation, followed by a second azo coupling to yield the disazo products (Scheme 1). Attempted diazotisations of **10c** and **11b** were unsuccessful, probably because of their insolubility in aqueous acid. The need for a two-stage process adds complexity to the synthesis of symmetrical derivatives. In contrast, however, it offers potential versatility due to the fact that unsymmetrical derivatives may be prepared using different coupling components at each stage, a feature not easily achieved in the case of diarylide yellow pigments based on DCB. The calcium and manganese salt pigments from **12a**–**12d** to **13** were prepared by reaction of the disodium salts with calcium or manganese chloride in aqueous solution at 95–99 °C. The particular metal (M) ion used in the structures represented in Figs. 11 and 12 is indicated in subsequent text and tables in this paper by the product codes **I** (2Na$^+$), **II** (Ca^{2+}) and **III** (Mn^{2+}).

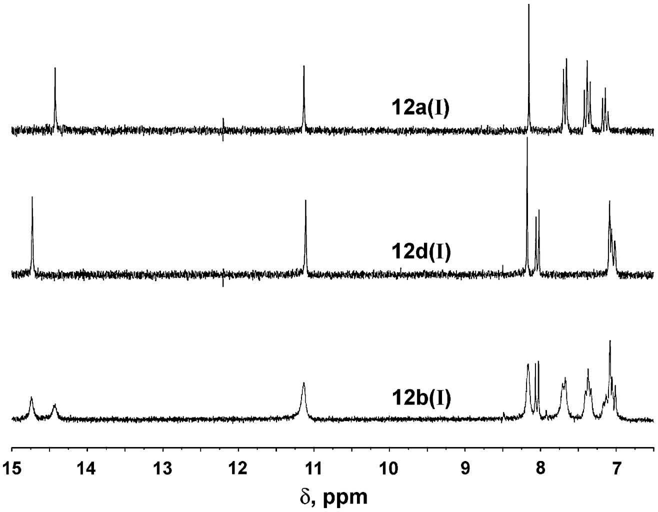

Fig. 13. ^{1}H NMR spectra of disodium salts **12aI**, **12bI** and **12dI**.

FTIR spectra for all metal-salts **12** and **13** and the ^{1}H NMR spectra for the disazo sodium salts demonstrate that in solid state and solution phases they exist in the bisketohydrazone tautomeric forms, structurally analogous to the diarylide yellow pigments by comparison of spectral data [14–17]. ^{1}H NMR data demonstrate clearly the symmetry of disodium salts **12a**(**I**), **12d**(**I**) and **13**(**I**). In contrast, there are two separate sets of signals in the aromatic region of the ^{1}H NMR spectra of disodium salts **12b**(**I**) and **12c**(**I**) consistent with each half of the molecule having a different substituent pattern in the terminal anilide rings and separate hydrazone NH signals. This is illustrated for the three of the disodium salts in Fig. 13. Compound **12a**(**I**) gives the signals expected for the terminal phenyl substituents and **12d**(**I**) gives the signals expected for the 2,4-dimethylphenyl groups with a single sharp NH signal. Unsymmetrical compound **12b**(**I**), which contains phenyl and 2,4-dimethylphenyl substituents shows the separate groups of aromatic signals (with some overlap), and separate hydrazone NH signals. While separate amide NH and phenylene ring aromatic signals are not resolved, the signals are broadened. UV/vis spectra of the yellow disodium salts **12a**(**I**)–**12d**(**I**) in DMF gave very similar λ_{max} values (442, 443, 445 and 445 nm, respectively). The most significant difference was the broader absorption band in the spectra of the unsymmetrical derivatives **12b**(**I**) and **12c**(**I**). The corresponding orange pyrazolone disodium salt **13**(**I**) gave a λ_{max} value of 485 nm.

3.2. *Assessment of pigment properties*

The technical properties of the new pigments were assessed in industrial alkyd/melamine paints, both in full strength and in white reductions, in comparison with the structurally analogous commercially important diarylide yellows and oranges **1a**–**1c**, **2a** and **2b** selected as standards. While these pigments are most

Table 1
Colour parameters for standard DCB-based commercial and 1,4-phenylenediamine-based analogues in full-strength industrial paints

Pigment	L^*	C^*	h (°)	Pigment	L^*	C^*	h (°)
1a (Y12)	76.80	83.23	80.08	**7a**	58.43	65.09	58.38
1b (Y13)	79.10	87.15	80.64	**7b**	55.25	58.56	57.20
1c (Y83)	72.58	85.90	67.80	**7c**	45.47	48.69	43.79
2a (O13)	56.42	74.84	43.32	**8a**	41.71	49.99	31.20
2b (O34)	50.64	68.41	38.13	**8b**	43.76	55.20	34.01

commonly used in printing inks, we believed that the aim of the present investigation merited their evaluation in a medium which was more demanding in terms of technical performance. The colour parameters for the DCB-based pigments, and the corresponding 1,4-phenylenediamine-based pigments **7a**–**7c**, **8a** and **8b** in full-strength paints are given in Table 1, with the corresponding data for 1:3 white reductions in Table 2.

In full-strength paints, all of the pigment derivatives **7** and **8** are darker, weaker, and redder in colour than the standard products. 1,4-Phenylenediamine-based pigments are also inferior colouristically to the corresponding DCB-based pigments in white reductions.

The metal-salt disazo pigments are much more interesting colouristically, and closer to the standard DCB-based pigments than the corresponding 1,4-phenylenediamine-based pigments in both full shade and white reduction(Tables 3 and 4). They are, in general, slightly darker and redder in full shade paint, although some derivatives have high chroma values. Unsymmetrical pigments **12b** and **12c** are noticeably duller than the symmetrical derivatives **12a** and **12d**, especially the calcium and manganese metal salts. This is consistent with the broader absorption bands in the solution UV/vis spectra. It is a general feature of colorants that symmetry leads to narrower bandwidths and brighter colours, a feature explained by minimising geometrical change on excitation from the ground state to the first excited state [19]. A notable example is the bright colour of copper phthalocyanine blue which is associated with its high molecular symmetry [20]. With pigments, a further factor may be that molecular asymmetry leads to less efficient crystal packing and a consequent deterioration in colouristics. A consistent trend in colour properties is that the sodium salts are the lightest in colour, followed by the calcium salt, and then the manganese salt, while the degree of redness follows the opposite trend.

The results from the solvent resistance tests are given in Table 5, assessed as degree of bleed from samples overpainted with white paint and quantified as a colour difference (ΔE) between the white layer and the overpainted layer. The standard diarylide pigments show some bleed in this paint system, although it is very small in the case of C.I. Pigment Yellow 83 (**1c**). 1,4-Phenylenediamine-based pigments have inferior solvent resistance, probably associated with the smaller molecular size, clearly unacceptable for this application. In contrast, certain of the metal-salt pigments have excellent overpaint fastness, especially the salts of **12a**, **12b** and **13** when compared with the standard pigments. The salts of **12d** show poor solvent fastness which may be due to crystal packing effects. Efficient molecular packing in the crystal structure is likely to lead to good solvent resistance and any structural feature causing disruption of crystal packing would lead to reduced solvent resistance.

The lightfastness results for the full-strength paints and the white reductions are given in Tables 6 and 7, respectively. In full-strength paints, the lightfastness of 1,4-phenylenediamine-based diarylide yellow pigments **7a**–**7c** is significantly inferior to the corresponding standards **1a**–**1c**. Interestingly, the pyrazolone

Table 2
Colour parameters for standard DCB-based commercial and 1,4-phenylenediamine-based analogues in 1:3 white reductions

Pigment	L^*	C^*	h (°)	Pigment	L^*	C^*	h (°)
1a (Y12)	83.94	70.68	85.40	**7a**	70.64	64.38	63.33
1b (Y13)	84.56	66.66	83.01	**7b**	69.81	60.84	64.85
1c (Y83)	78.98	77.31	74.25	**7c**	64.54	54.38	64.11
2a (O13)	65.26	65.23	43.01	**8a**	53.87	52.59	29.96
2b (O34)	60.30	64.52	40.12	**8b**	56.94	57.56	36.50

Table 3
Colour parameters for 2,5-phenylenediamine-1,6-disulphonic acid-based metal-salt disazo pigments in full-strength industrial paints

Compound	$2Na^+$ (**I**)			Ca^{2+} (**II**)			Mn^{2+} (**III**)		
	L^*	C^*	h (°)	L^*	C^*	h (°)	L^*	C^*	h (°)
12a	72.30	80.35	73.32	72.20	81.41	71.56	69.05	76.96	68.24
12b	67.79	75.13	68.30	64.56	74.93	61.48	63.83	69.83	62.37
12c	61.67	68.64	64.25	53.22	61.26	48.53	51.45	57.60	48.34
12d	69.13	73.41	73.70	66.55	72.24	67.19	65.11	72.28	63.34
13	50.22	64.84	37.52	35.89	45.71	23.06	35.56	39.81	23.47

Table 4
Colour parameters for 2,5-phenylenediamine-1,6-disulphonic acid-based metal-salt disazo pigments in 1:3 white reductions

Compound	$2Na^+$ (**I**)			Ca^{2+} (**II**)			Mn^{2+} (**III**)		
	L^*	C^*	h (°)	L^*	C^*	h (°)	L^*	C^*	h (°)
12a	79.17	75.88	78.15	78.48	76.30	76.75	76.94	72.24	74.65
12b	78.08	64.52	77.33	74.26	68.93	67.50	74.46	68.02	69.97
12c	76.30	61.81	78.65	70.89	60.29	66.65	72.57	43.03	64.28
12d	79.79	63.52	83.19	77.10	64.64	75.57	74.99	66.45	70.42
13	60.54	64.15	44.10	45.35	47.54	20.55	41.86	39.35	13.42

Table 5
Colour difference between overpainted samples and white overlayer for standard DCB-based commercial and 1,4-phenylenediamine-based analogues in industrial paints

Pigment	ΔE	Pigment	ΔE	Metal-salt pigment	ΔE (2Na, **I**)	ΔE (Ca, **II**)	ΔE (Mn, **III**)
1a (Y12)	10.6	**7a**	46.2	**12a**	0.2	0.4	0.4
1b (Y13)	3.3	**7b**	33.4	**12b**	0.4	0.6	0.5
1c (Y83)	1.0	**7c**	13.6	**12c**	1.3	1.2	1.2
2a (O13)	8.2	**8a**	30.4	**12d**	11.7	12.4	10.9
2b (O34)	4.4	**8b**	13.2	**13**	0.8	1.0	1.1

Table 6
Lightfastness of standard DCB-based commercial pigments and 1,4-phenylenediamine-based analogues in full-strength industrial paints assessed by colour difference before and after exposure for 350 h

Pigment	ΔE	Pigment	ΔE	Metal-salt pigment	ΔE (2Na, **I**)	ΔE (Ca **II**)	ΔE (Mn **III**)
1a (Y12)	2.0	**7a**	53.3	**12a**	28.6	7.6	4.5
1b (Y13)	2.7	**7b**	26.3	**12b**	22.9	11.2	10.2
1c (Y83)	1.0	**7c**	20.7	**12c**	8.0	1.7	3.8
2a (O13)	7.8	**8a**	5.4	**12d**	2.5	5.4	7.1
2b (O34)	5.8	**8b**	4.2	**13**	2.3	5.4	14.3

Table 7
Lightfastness of standard DCB-based commercial pigments and 1,4-phenylenediamine-based analogues in 1:3 white reduction industrial paints assessed by colour difference before and after exposure for 350 h

Pigment	ΔE	Pigment	ΔE	Metal-salt pigment	ΔE (2Na, **I**)	ΔE (Ca **II**)	ΔE (Mn **III**)
1a (Y12)	28.1	**7a**	60.6	**12a**	60.9	58.9	54.2
1b (Y13)	3.4	**7b**	56.2	**12b**	51.1	50.9	42.7
1c (Y83)	1.5	**7c**	49.1	**12c**	35.5	23.1	18.0
2a (O13)	25.7	**8a**	51.8	**12d**	30.0	28.0	29.0
2b (O34)	11.8	**8b**	54.4	**13**	42.7	18.5	29.0

Table 8
Heat stability of standard DCB-based commercial pigments and 1,4-phenylenediamine-based analogues

Pigment	ΔE	Pigment	ΔE	Metal-salt pigment	ΔE (2Na, **I**)	ΔE (Ca **II**)	ΔE (Mn **III**)
1a (Y12)	0.28	**7a**	0.24	**12a**	1.62	0.39	0.97
1b (Y13)	0.19	**7b**	0.16	**12b**	0.25	0.48	0.22
1c (Y83)	0.28	**7c**	0.97	**12c**	0.74	0.20	0.49
2a (O13)	0.40	**8a**	0.30	**12d**	0.14	1.99	1.47
2b (O34)	0.42	**8b**	0.29	**13**	0.20	2.82	4.18

pigments **8a** and **8b** have slightly better fastness to light than the corresponding standards **2a** and **2b**. The full-strength paints containing the metal-salt disazo pigments gave variable lightfastness, but with some, e.g., **12c**(**II**), **12d**(**I**) and **13**(**I**) being comparable with corresponding standards. In 1:3 white reductions, the new pigments derived from 1,4-phenylenediamine derivatives generally showed inferior lightfastness compared with the standards.

To test the heat stability of each compound, drawdowns of the 1:3 white reduction paints were stoved for 15 min and 60 min and the heat stability assessed as the colour difference (ΔE) between the two sets of drawdowns. The results are given in Table 8. Most pigments would be deemed to have adequate heat stability ($\Delta E < 1$) for this application except for **12a**(**I**), **12d** and **13** (Ca^{2+} and Mn^{2+} salts in each case). A curious observation is that the unsymmetrical disazo metal-salt pigments (**12b** and **12c**) have, in general, slightly improved heat stability properties compared with the symmetrical compounds.

4. Conclusions

The pigments reported in this study were, in general, reasonably easy to synthesise in moderate to high yields. Of the diamines investigated as potential replacements for DCB, 2,5-phenylenediamine-1,6-disulphonic acid is of particular interest as it is likely to be of low toxicity, non-carcinogenic, non-mutagenic, and potentially low cost. 1,4-Phenylenediamine-based pigments were generally somewhat inferior to the industrial DCB-based analogues colouristically, in solvent resistance and in lightfastness. The synthesis of disazo metal-salt pigments based on 2,5-phenylenediamine-1,6-disulphonic acid is complicated by the requirement for a two-stage process, although this offers the advantage of an easy route to unsymmetrical derivatives. Generally, the colouristic properties are slightly inferior to the DCB derivatives. Lightfastness is in some cases comparable in full strength although inferior in tint, while the solvent resistant is better, as expected for metal-salt type pigments. It is worth noting that the standard pigments used for comparison are optimised commercial products, and it may well be possible to further optimise the physical properties of the new pigments, for example, by control of particle size and morphology and by surface treatment, for improved colour properties and technical performance.

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