

## Research Article

# Diphenyl (4'-(Aryldiazenyl)biphenyl-4-ylamino) (pyridin-3-yl)methylphosphonates as Azo Disperse Dyes for Dyeing Polyester Fabrics

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Diphenyl (4'-aminobiphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (**1**) was synthesized in 88% yield from reaction of pyridine-3-carboxaldehyde with benzidine and triphenylphosphite in the presence of titanium tetrachloride as a catalyst. Diazotization of **1** gave the corresponding diazonium salt **2** which was coupled with several hydroxyl or amino compounds to give the corresponding azo dyes **3–8** in 82–88% yields after crystallization. The dyes produced were applied to polyesters as disperse dyes and their fastness properties were elevated.

## 1. Introduction

The unique biological activities and characteristic chemical structures have made synthesis  $\alpha$ -aminophosphate derivatives attractive over the years [1]. Synthesis of  $\alpha$ -aminophosphates provides numerous compounds with various pharmacological activities [2–17].

The growth of the spinning and weaving industry prompted researchers to develop synthetic dyes to satisfy different industrial demands [18]. The most important class of synthetic dyes is azo dyes that form along with pigments the largest group of synthetic colorants that play prominent role in various applications.

As part of our continuing interest in organic synthesis [19–22], we have developed efficient syntheses of various substituted heterocycles [23–38]. Also, we have reported a simple and convenient approach for the synthesis of a series of azodisperse dyes [39]. We now report the successful synthesis of new azodisperse dyes containing  $\alpha$ -aminophosphonates and their application for dyeing polyester fabrics.

## 2. Experimental

Melting point determinations were performed by the open capillary method using an Electrothermal MEL-TEMP II apparatus and are reported uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 Spectrophotometer using KBr disc technique. <sup>1</sup>H NMR spectra were recorded on a Bruker AC400 spectrometer operating at 400 MHz. The spectra were recorded in DMSO-*d*<sub>6</sub>. Chemical shifts  $\delta$  are reported in parts per million (ppm) relative to TMS and coupling constants *J* are in Hz and have been rounded to the nearest whole number. Assignments of signals are based on integration values and expected chemical shift values and have not been rigorously confirmed. EI mass spectra were recorded at energy 70 eV with a 7070 EQ mass spectrometer. Microanalyses were performed by analytical service at both the Universities of Tanta and Cairo, Egypt. Analytical thin layer chromatography (TLC) was performed on EM silica gel F<sub>254</sub> sheet (0.2 mm) with chloroform/acetone (5:2 by volume) as a developing eluent. The spots were detected with

UV Lamp Model UV GL-58. Reagents and solvents were used from commercial sources without purification.

**2.1. Synthesis of Diphenyl (4'-(Aminobiphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (1).** A mixture of pyridine-3-carboxaldehyde (1.07 g, 10 mmol), benzidine (1.84 g, 10 mmol), triphenylphosphite (3.72 g, 12 mmol), and titanium tetrachloride (0.19 g, 1 mmol) in dichloromethane (10 mL) was stirred at room temperature for 26 h. The solvent was removed under reduced pressure, and the residue obtained was treated with methanol (20 mL) and then filtered to remove the solid materials. A mixture of water (10 mL) and dichloromethane (10 mL) was added to the filtrate. The organic layer was separated and washed with water (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and removed under reduced pressure to give the crude product which was recrystallized from ethanol to give pure **1** in 88% yield as colorless solid; m.p. 120–122°C. IR (KBr,  $\nu_{\text{max}}$ ): 3329, 1597, 823  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  10.17 (br s, exch., 1 H, NH), 9.15–6.76 (m, 22 H, aromatic), 5.16 (d,  $J$  = 16 Hz, 1 H, CH), 3.97 (s, exch., 2 H,  $\text{NH}_2$ ). MS ( $m/z$ , %): 507 ( $\text{M}^+$ , 5), 449 (12), 390 (22), 314 (35), 265 (44), 396 (5), 225 (100), 214 (12), 168 (11). Analyses Calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_3\text{O}_3\text{P}$ : C, 71.00; H, 5.16; N, 8.28; P, 6.10%. Found: C, 71.12; H, 4.94; N, 8.01; P, 6.15%.

**2.2. General Procedure for the Synthesis of Compounds 3–8.** A cold (0°C) solution of sodium nitrate (0.76 g, 11 mmol) in  $\text{H}_2\text{O}$  (10 mL) was added gradually to a cold (0°C) suspension of **1** (5.07 g, 10 mmol) in conc. HCl (5 mL). The diazonium salt **2** thus obtained was added with continuous stirring to a cold (0°C) solution of coupler (10 mmol) in aqueous NaOH solution (10%, 15 mL). The mixture was stirred at 0°C for 30 min and the dye obtained was filtered, washed with  $\text{H}_2\text{O}$ , dried, and crystallized from ethanol to give products **3–8**.

**2.2.1. Diphenyl (4'-((4-Hydroxynaphthalen-1-yl)diazenyl)biphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (3).** Yield 88%; rubine; m.p. 179–181°C. IR (KBr,  $\nu_{\text{max}}$ ): 3494, 1613, 1581, 1323, 893  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.10 (s, exch., 1 H, OH), 8.73 (br s, exch., 1 H, NH), 8.50–7.21 (m, 28 H, Ar-H), 6.95 (d,  $J$  = 12 Hz, 1 H, CH). MS ( $m/z$ , %): 662 ( $\text{M}^+$ , 3), 613 (2), 531 (3), 439 (59), 410 (4), 396 (5), 362 (29), 273 (12), 98 (100). Analyses Calcd. for  $\text{C}_{40}\text{H}_{31}\text{N}_4\text{O}_4\text{P}$ : C, 72.50; H, 4.72; N, 8.45; P, 4.67%. Found: C, 72.62; H, 4.74; N, 8.41; P, 4.65%.

**2.2.2. Diphenyl (4'-((2-Hydroxynaphthalen-1-yl)diazenyl)biphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (4).** Yield 84%; dark red; m.p. 190–193°C; IR (KBr,  $\nu_{\text{max}}$ ): 3337, 1613, 1580, 1325, 890  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.09 (s, exch., 1 H, OH), 8.81 (br s, exch., 1 H, NH), 8.72–7.43 (m, 28 H, Ar-H), 6.95 (d,  $J$  = 12 Hz, 1 H, CH). MS ( $m/z$ , %): 662 ( $\text{M}^+$ , 4), 613 (4), 531 (6), 439 (66), 410 (6), 396 (4), 362 (32), 273 (15), 98 (100). Analyses Calcd. for  $\text{C}_{40}\text{H}_{31}\text{N}_4\text{O}_4\text{P}$ : C, 72.50; H, 4.72; N, 8.45; P, 4.67%. Found: C, 72.60; H, 4.77; N, 8.39; P, 4.69%.

**2.2.3. Diphenyl (4'-((2,4-Dihydroxyphenyl)diazenyl)biphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (5).** Yield 89%; red violet; m.p. 171–173°C. IR (KBr,  $\nu_{\text{max}}$ ): 3332, 1610, 1490, 1320, 896  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.11 (s, exch., 1 H, OH), 8.81 (br s, exch., 1 H, NH), 8.73 (s, exch., 1 H, OH), 8.50–7.08 (m, 25 H, Ar-H), 6.92 (d,  $J$  = 13 Hz, 1 H, CH); MS ( $m/z$ , %): 628 ( $\text{M}^+$ , 3), 564 (4), 514 (3), 436 (25), 362 (100), 282 (28), 273 (12). Analyses Calcd. for  $\text{C}_{36}\text{H}_{29}\text{N}_4\text{O}_5\text{P}$ : C, 68.78; H, 4.65; N, 8.91; P, 4.93%. Found: C, 68.62; H, 4.84; N, 8.86; P, 4.95%.

**2.2.4. Diphenyl (4'-((5-Amino-2-hydroxyphenyl)diazenyl)biphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (6).** Yield 84%; reddish burgundy; m.p. 149–152°C; IR (KBr,  $\nu_{\text{max}}$ ): 3399, 1613, 1582, 1327, 884  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.09 (s, exch., 1 H, OH), 8.81 (br s, exch., 1 H, NH), 8.72–6.93 (m, 25 H, Ar-H), 6.63 (d,  $J$  = 13 Hz, 1 H, CH), 6.37 (s, exch., 2 H,  $\text{NH}_2$ ). MS ( $m/z$ , %): 627 ( $\text{M}^+$ , 3), 413 (2), 362 (100), 282 (38), 273 (13), 152 (38). Analyses Calcd. for  $\text{C}_{36}\text{H}_{30}\text{N}_5\text{O}_4\text{P}$ : C, 68.89; H, 4.82; N, 11.16; P, 4.94%. Found: C, 68.62; H, 4.94; N, 11.01; P, 4.85%.

**2.2.5. 7-Amino-3-((4'-((diphenoxyphosphoryl)(pyridin-3-yl)methylamino)biphenyl-4-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic Acid (7).** Yield 83%; burgundy; m.p. 161–163°C. IR (KBr,  $\nu_{\text{max}}$ ): 3424, 1675, 1519, 1299, 1163, 892  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ): 9.09 (s, exch., 1 H, OH), 8.90 (s, exch., 1 H,  $\text{SO}_3\text{H}$ ), 8.80 (br s, 1 H, NH), 8.72–6.93 (m, 26 H, Ar-H), 6.75 (d,  $J$  = 12 Hz, 1 H, CH), 6.83 (s, exch., 2 H,  $\text{NH}_2$ ). MS ( $m/z$ , %): 757 ( $\text{M}^+$ , 6), 515 (39), 439 (15), 362 (72), 282 (100), 273 (11). Analyses Calcd. for  $\text{C}_{40}\text{H}_{32}\text{N}_5\text{O}_7\text{PS}$ : C, 63.40; H, 4.26; N, 9.24; P, 4.09%. Found: C, 63.62; H, 4.24; N, 9.21; P, 4.15%.

**2.2.6. Diphenyl (4'-((2-Amino-5-methylphenyl)diazenyl)biphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (8).** Yield 82%; buff; m.p. 201–203°C. IR (KBr,  $\nu_{\text{max}}$ ): 3408, 1612, 1582, 1323, 890  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 9.09 (br s, exch., 1 H, NH), 8.80–6.49 (m, 25 H, Ar-H), 5.65 (d,  $J$  = 12 Hz, 1 H, CH), 5.26 (s, exch., 2 H,  $\text{NH}_2$ ), 2.30 (s, 3 H,  $\text{CH}_3$ ). MS ( $m/z$ , %): 625 ( $\text{M}^+$ , 9), 442 (15), 362 (100), 282 (97), 273 (40), 152 (95). Analyses Calcd. for  $\text{C}_{37}\text{H}_{32}\text{N}_5\text{O}_3\text{P}$ : C, 71.03; H, 5.16; N, 11.19; P, 4.95%. Found: C, 71.02; H, 5.04; N, 11.01; P, 4.85%.

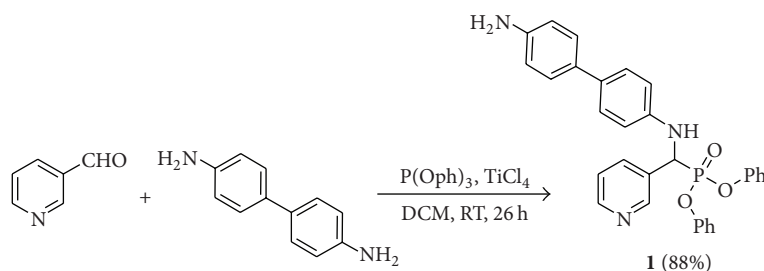
**2.3. Dyeing Procedure.** The fabric was dyed with dye (2%; calculated by weight of the fabric) and Avolan IS (1%; Bayer AG, Germany) as dispersing agent, kept at a liquor ratio of 20 : 1. The process was started at 60°C; the temperature was then raised to 130°C over 30 min and maintained there for 1 h. After cooling, the fabric was removed and then treated with a solution of  $\text{NaHSO}_4$  (2%), NaOH (2%), and the dispersing agent Avolan IS (0.1%) at 70°C for 30 min. Finally, the fabric was rinsed and dried at 60°C.

**2.3.1. Colour Fastness Tests.** The results are collected in Table 1.

TABLE 1: Fastness properties of dyes 3–8.

| Compound | Washing | Perspiration |        | Rubbing |     | Sublimation |    | Light (40 h) |
|----------|---------|--------------|--------|---------|-----|-------------|----|--------------|
|          |         | Acid         | Alkali | Dry     | Wet | Alt         | St |              |
| 3        | 5       | 4            | 5      | 4       | 5   | 5           | 4  | 7            |
| 4        | 5       | 5            | 4      | 5       | 4   | 5           | 4  | 6            |
| 5        | 4       | 5            | 5      | 5       | 4   | 5           | 5  | 5            |
| 6        | 5       | 5            | 4      | 4       | 4   | 4           | 5  | 6            |
| 7        | 5       | 4            | 5      | 4       | 5   | 4           | 4  | 5            |
| 8        | 5       | 5            | 5      | 5       | 5   | 5           | 5  | 6            |

Alt: alteration, St: staining, rate for light fastness: 5–8 (acceptable), 1–4 (not acceptable); rate for different fastness: 4–5 (acceptable), 1–3 (not acceptable).



SCHEME 1: Synthesis of diphenyl (4'-aminobiphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (1).

**Fastness to Washing.** A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton fabric, all of equal length, and then washed at 50°C for 30 min.

**Fastness to Perspiration.** The samples were prepared by stitching a piece of dyed polyester fabric between two pieces of undyed cotton fabric, all of equal length, and then immersed in the acid or alkaline solution for 30 min. The acid solution (pH = 3.5) contained sodium chloride (10 g/L), lactic acid (1 g/L), disodium orthophosphate (1 g/L) and histidine monohydrochloride (0.25 g/L). The alkaline solution (pH = 8) contained sodium chloride (10 g/L), NH<sub>4</sub>Cl (4 g/L), disodium orthophosphate (1 g/L), and histidine monohydrochloride (0.25 g/L).

**Fastness to Rubbing.** The dyed polyester fabric was placed on the base of the Crockmeter, so that it rested flat on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was allowed to slide on the tested fabric back and forth twenty times by making ten complete turns of the crank according to the international standard procedure. For the wet rubbing test, the testing squares were thoroughly immersed in distilled water. The remaining procedure was the same as in the dry test.

**Fastness to Sublimation.** Sublimation fastness was measured with an iron tester (Yasuda no. 138). The samples were prepared by stitching a piece of dyed polyester fabric between two pieces of undyed polyester, all of equal length, and then treated at 180°C and 210°C each for 1 min.

**Fastness to Light.** Light fastness was determined by exposing the dyed polyester on a Xenotest 150 (Original Hanau, chamber temperature 25–30°C, black panel temperature 60°C,

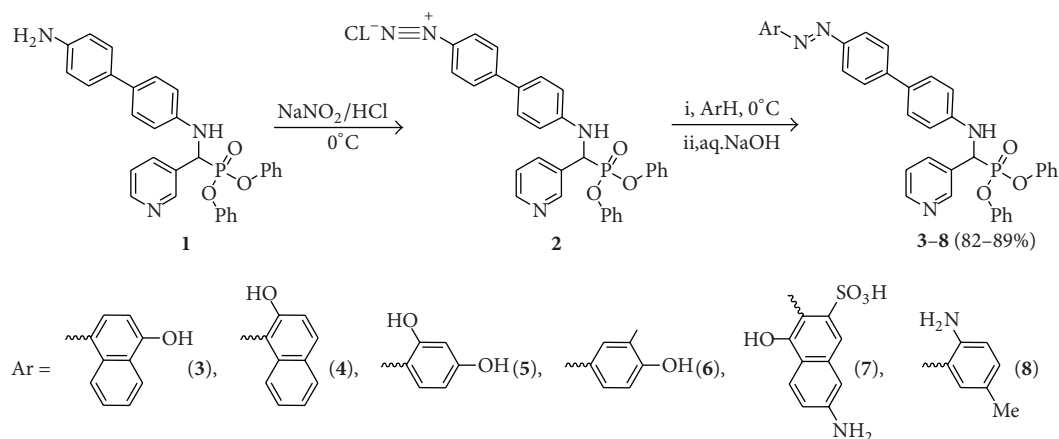
relative humidity 50–60%, and dark glass (UV filter system)) for 40 h.

### 3. Result and Discussion

Diphenyl (4'-aminobiphenyl-4-ylamino)(pyridin-3-yl)methylphosphonate (1) was synthesized in 88% yield after crystallization from reaction of pyridine-3-carboxaldehyde, benzidine, and triphenylphosphite in the presence of a catalytic quantity of titanium tetrachloride (TiCl<sub>4</sub>) as a Lewis acid in dichloromethane (DCM) for 26 h at room temperature (Scheme 1). The structure of 1 was confirmed by elemental analysis, IR, <sup>1</sup>H NMR, and mass spectral data (see Section 2 for details).

Diazotization of 1 was performed by using a mixture of sodium nitrite and hydrochloric acid to produce the corresponding diazonium salt 2. Coupling of 2 with several hydroxy or amino compounds, such as 1-naphthol, 2-naphthol, resorcinol, 2-aminophenol, 7-amino-4-hydroxynaphthalene-2-sulfonic acid, and 4-toluidine in aqueous sodium hydroxide solution afforded the corresponding diphenyl pyridin-3-yl(4'-(aryldiazenyl)biphenyl-4-ylamino)methylphosphonates 3–8 in high yields (82–89%; Scheme 2).

The structures of diazo dyes 3–8 were confirmed by various spectroscopic techniques including IR, <sup>1</sup>H NMR and mass spectral data and their purities were confirmed by elemental analyses. The IR spectra of 3–8 are characterized by the presence of absorption bands within the 3494–3332 cm<sup>-1</sup> region corresponding to the stretching vibrations of the NH and/or OH groups. The absorption bands at the 1582–1490 cm<sup>-1</sup> region are due to the symmetric stretching



SCHEME 2: Synthesis of azo dyes 3–8.

vibrations of the azo group. The bands with the 1327–1299 and 896–884  $\text{cm}^{-1}$  regions are due to the stretching vibrations of the P=O and P–O–C groups, respectively. The  $^1\text{H}$  NMR, spectra showed a characteristic CH doublet signal in the 6.95–5.65 ppm region. They also showed an exchangeable singlet signal that resonated in the 9.09–8.80 ppm region due to the NH proton. The structures of diazo dyes 3–8 were confirmed further by mass spectral data. The electron impact mass spectra indicated the presence of molecular ion peaks in all cases. Moreover, the elemental analyses of 3–8 were consistent with the suggested structures and confirm the purities of the products (see Section 2 for details).

**3.1. Dyeing of Polyester Fabrics and Dyeing Properties.** Most influences that can affect fastness are light, washing, heat, perspiration, and atmospheric pollution. Conditions of such tests are chosen to correspond closely to the treatments employed in manufacture and of ordinary use conditions [40]. Results are given after usual matching of the tested samples against standard reference (the greyscale) [40]. The results obtained are shown in Table 1. The results revealed that azo dyes 3–8 have good fastness properties.

## 4. Conclusions

A set of six useful disperse dyes 3–8 were synthesised by azo coupling. The dyes were investigated for their dyeing characteristics on polyester and showed good washing, perspiration, rubbing, sublimation and light fastness. The remarkable degree of brightness after washings is indicative of good penetration and the excellent affinity of these dyes for the fabric due to the accumulation of polar groups.

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