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New Phosphonic Acid Reactive Dyes for Cotton†

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SUMMARY

The synthesis of some new azo reactive dyes which contain a phosphonic acid group in a pendant chain of the coupling component is described. Four phosphonic acid couplers have been prepared and coupled to two different diazo compounds to produce eight reactive dyes which have good washfastness properties once fixed on cotton.

The structures of the dyes were confirmed with the aid of ^{1}*H-NMR.*

1 INTRODUCTION

About 90 years ago, Cross and Bevan attempted[1] to generate a dye covalently bonded to cellulose by elaborating the phenyl group of cellulose benzoate in a series of four steps (nitration, reduction, diazotization, and diazo coupling). It was not until 1956, however, that Rattee, then working for ICI, developed the first truly commercial reactive dyes. These dyes are known today as the Procion dyes and used the dichlorotriazinyl group as the reactive function. Since that time numerous reactive dye types (e.g. Cibacron, Levafix E, Reacton, Drimarene and Reactofil) have been developed which contain labile halogens on nitrogen heterocyclic systems as leaving groups for the generation of a covalent linkage to the cotton fiber. Others which enjoy commercial success contain a leaving group other than a halogen such as the vinyl sulfone (Remazol) and methylsulfonyl (Levafix P).

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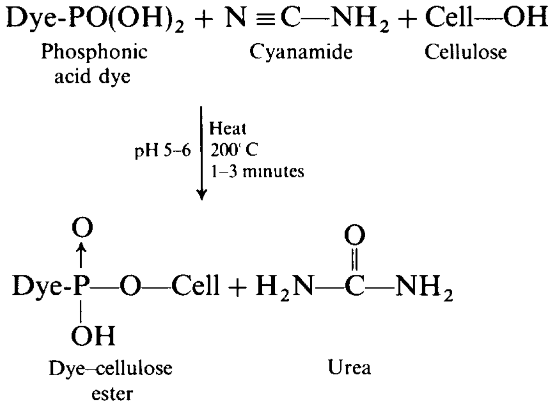
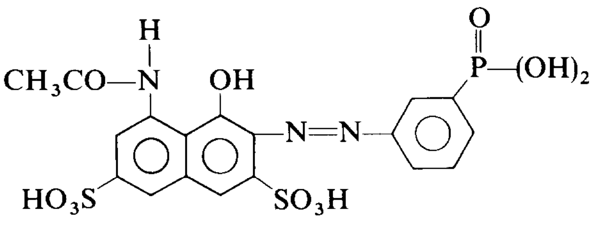
The newest of the cellulose reactive dyes prepared jointly by ICI and Burlington Industries contain one or more phosphonic groups which form a phosphonate linkage to the cellulose molecule under weakly acidic (pH 5–6) conditions rather than the alkaline conditions used for other reactives. These dyes also require the use of cyanamide (cf. Scheme 1) or the less toxic dicyandiamide to facilitate fiber attachment.[2] But perhaps more importantly they have been reported[2] to give a much higher degree of fiber fixation than any of their predecessors. Typical dyes of this type are the monophosphonic acid **1** and the diphosphonic acid derivative **2**, in which the phosphonic acid moiety is attached directly to the aromatic ring of a potential diazo component.



Scheme 1. The cyanamide fixation of phosphonic acid reactive dyes.



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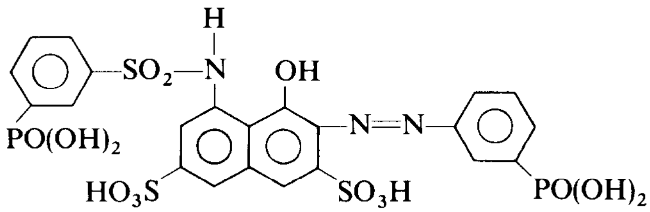

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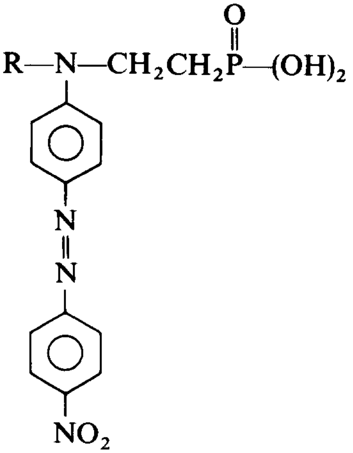
We report here the synthesis of dyes of type **3** and **4**, as a preliminary assessment of some new phosphonic acid azo reactive dyes in which the phosphonic acid group is built into the coupler residue. Variations in group R were made to determine the effect of alkyl substituent size on the reactivity of the PO_3H_2 group.



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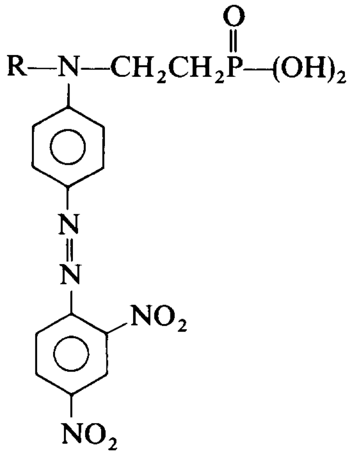

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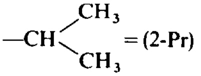
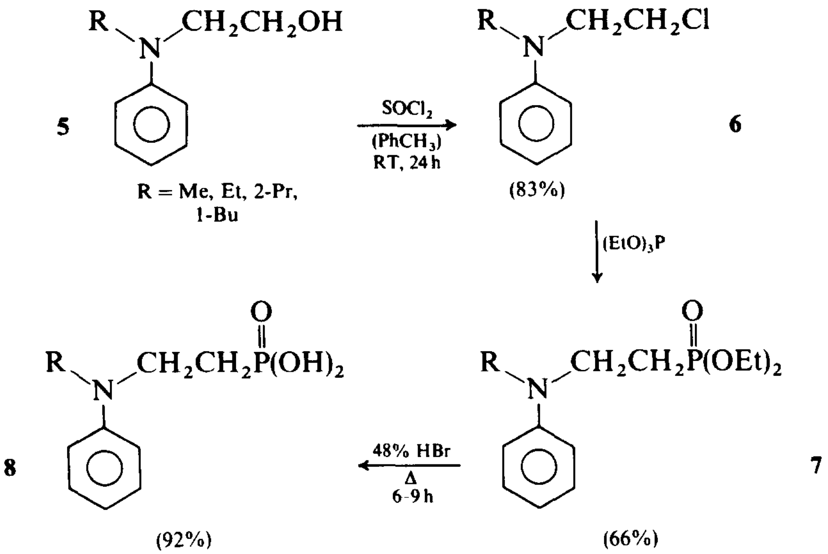
Where R is: a. $—CH_3$ = (Me)
b. $—C_2H_5$ = (Et)
c. 
$—CH(CH_3)_2$ = (2-Pr)
d. $—(n\text{-}C_4H_9)$ = (1-Bu)

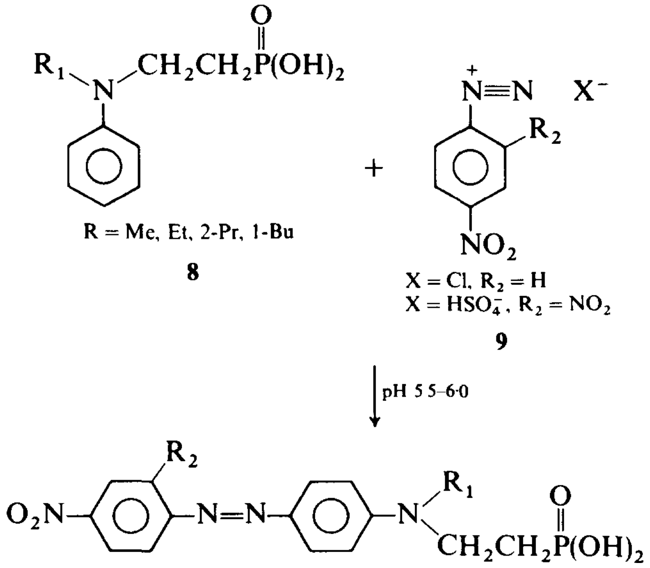
2 RESULTS AND DISCUSSION

The coupling components were prepared from commercially available *N*-hydroxyethylanilines **5** as outlined in Scheme 2. The hydroxyl group was replaced by a chloro group using the method of Boon,[3] and the chloroethyl derivatives were purified with the aid of a falling film still (Kontes Glass Co., PO Box 729, Vineland, New Jersey 08360, USA). The pure halides were then heated with triethyl phosphite to produce the phosphonate esters **7**. This latter step is the well-known Michaelis–Arbuzov reaction.[4–6] The phosphonic acid derivatives **8** were generated from the acid hydrolysis of the corresponding esters. The average yields obtained for each step of the sequences are shown in Scheme 2.

The dyes shown in Scheme 3 were prepared by diazotization of 4-nitroaniline in HCl and of 2,4-dinitroaniline in H_2SO_4 and coupling to compounds **8** at pH 5·5–6·0 for 2–3 h. The crude dyes were purified by flash chromatography,[7] and their structures were confirmed from ^{1}H-NMR



Scheme 2. Preparation of phosphonated coupling components.



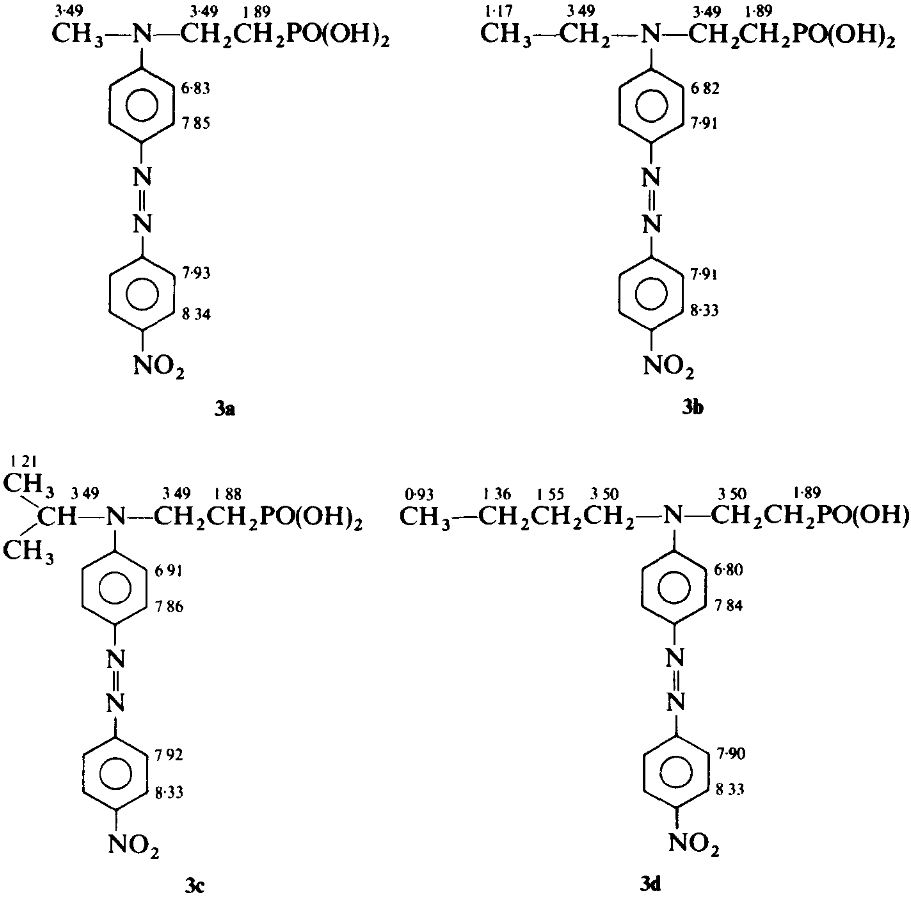
	R_1	R_2	
3 a.	R_1 = Me,	R_2 = H	(67%)
b.	R_1 = Et,	R_2 = H	(90%)
c.	R_1 = 2-Pr,	R_2 = H	(67%)
d.	R_1 = 1-Bu,	R_2 = H	(83%)
4 a.	R_1 = Me,	R_2 = NO_2	(81%)
b.	R_1 = Et,	R_2 = NO_2	(92%)
c.	R_1 = 2-Pr,	R_2 = NO_2	(67%)
d.	R_1 = 1-Bu,	R_2 = NO_2	(94%)

Scheme 3. Synthesis of new phosphonic acid group containing azo dyes.

spectra recorded on a 250 MHz spectrometer. The NMR δ values observed for the various protons are shown in Figs 1 and 2. The spectra were fully consistent with the structures for the dyes.

Solutions of dyes **3** in H_2O at pH 9 gave visible spectra having λ_{max} in the range 510–520 nm and similar solutions of **4** afforded visible spectra having a λ_{max} in the range 540–550 nm. The molar extinction coefficients were about 25 000 for **3**, and about 35 000 for **4**. All compounds showed λ_{max} in the range 510–520 nm when dissolved in acetone:H_2O (50:50) at pH 1.

A 1% shade of each dye was applied to 100% cotton fabric from a pad bath, and the dried fabric samples were treated at high temperature to fix the dye. The fabrics were then soaped to remove unfixed surface dye, and subjected to three colorfastness tests.[8] Each dye was found to have very good washfastness and crocking fastness in the AATCC Test Method



3a **3b** **3c** **3d**

Fig. 1. Assignment of the δ values observed in the ^{1}H-NMR spectra of dyes **3a**–**3d**.

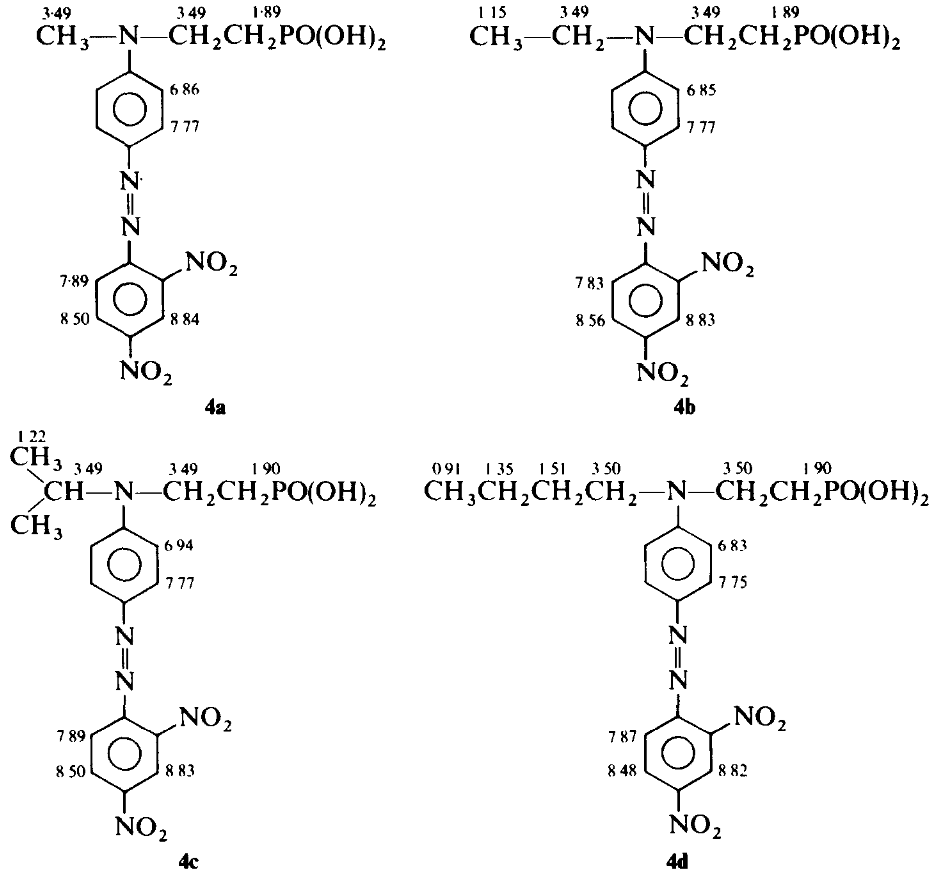


Fig. 2. Assignment of the δ values observed in the ^{1}H-NMR spectra of dyes **4a–4d**.

116–197. However, each had poor resistance to fading by light in the AATCC Test Method 16A-1977 which employs continuous light from a carbon-arc lamp.

3 EXPERIMENTAL

3.1 General

The ^{1}H-NMR and visible spectra were recorded on a Bruker 250 spectrometer and a Perkin–Elmer UV–visible spectrophotometer Model 559A, respectively. The crockfastness measurements were obtained using a standard rotary vertical crockmeter, the fastness to washing was assessed using an Atlas L-2-Q Launder-Ometer, and the fastness to light was determined using an Atlas FAD-R carbon arc fadeometer. The dye solutions were applied to the cotton fabrics from a Butterworth pressure pad onto 5·0 g samples at a wet pickup of 100%. The dyes were thermofixed in a Despatch oven at 210°C for 1 min, and the resulting fabrics were scoured at 80°C in a 0·5% solution of Barasol BR-M.

The phenylethanolamines which were used as starting materials in the preparation of the coupling components were obtained from Emery Industries, Inc., Mauldin, South Carolina, USA. *N*-(2-Chloroethyl)-*N*-ethylaniline was obtained from Emery Industries, Inc., Lock Haven, Pennsylvania, USA.

3.2 Synthesis of the *N*-chloroethylanilines 6

A mixture of 1 mol of the appropriate phenylethanolamine (**5**) and 400 ml of toluene was stirred at 2–4°C while a solution of $SOCl_2$ (1·5 mol) in 100 ml of toluene was added dropwise. The reaction was then allowed to warm to room temperature, stirred for 24 h and the mixture poured into 300 ml of H_2O; the pH was adjusted to 9 with 40% NaOH. The toluene layer was washed several times with H_2O, dried ($MgSO_4$), and concentrated to give the crude β-chloroethylanilines. The products were purified by high-vacuum distillation with the aid of a falling film still to give a final yield of 40% for **6b** (R = Me; b.p. 64–66°C, 0·01 mm), 53% for **6c** (R = 2-Pr; b.p. 92–95°C, 0·01 mm), and 40% for **6d** (R = Bu; b.p. 95–98°C, 0·01 mm). The yields of pure product were increased to 80–85% using flash chromatography to avoid losses due to thermal decomposition during distillation.

3.3 Synthesis of the phosphonate esters 7

A mixture of 1 mol of the appropriate chloroethylaniline (**5**) and 2 mol of triethyl phosphite was stirred under reflux for 48 h. Excess triethyl phosphite was removed (with heating) at the aspirator, and the phosphonates were collected at 0·02 mm to give **7a** (R = Me; 49%, b.p. 170°C), **7b** (R = Et; 39%, b.p. 156°C), **7c** (R = 2-Pr; 40%, b.p. 180°C), and **7d** (R = Bu; 66%, b.p. 195°C). Each compound exhibited a P=O peak in the range 1150–1170 cm^{-1} in the IR spectrum. The yields of the pure phosphonate ester could be improved to 65–70% using flash chromatography as the method of purification.

3.4 Synthesis of the phosphonic acids 8

The phosphonates (**7**, 0·035 mol) were stirred at the boil with 162 g (2·0 mol) of 48% HBr for 6–9 h. The reaction mixture was concentrated to 50 ml at the aspirator, diluted with 200 ml of H_2O, and the pH of the resulting mixture was adjusted to 9 with 40% NaOH. The cloudy solution was extracted with Et_2O to remove a small amount of unhydrolyzed ester. The aqueous part was acidified to Congo Red test paper and the precipitate was collected by vacuum filtration. The dried phosphonic acids were obtained in good yields: **8a** (R = Me; 90%), **8b** (R = Et; 92%), **8c** (R = 2-Pr; 63%), and **8d** (R = Bu; 73%). No further purification seemed necessary based on TLC and IR analyses.

3.5 Synthesis of azo dyes from compounds 3a–3d

Powdered 4-nitroaniline (3·08 g, 0·022 mol) was stirred with 80 ml of 10% HCl until a clear solution was obtained (slight warming was required). The solution was cooled to 3°C and a solution of $NaNO_2$ (1·54 g, 0·022 mol) in 50 ml H_2O was added, maintaining the temperature below 5°C. The solution was stirred for an additional 30 min and was added to a freshly prepared aqueous solution (100 ml) containing the phosphonic acids **8** (0·022 mol) at pH 5. The pH of the reaction was maintained near 5 by the periodic addition of 30% NaOH. After addition of the diazonium salt, the reaction was stirred cold for 30 min, and the pH was adjusted to 3·5 to precipitate the dyes. These were filtered, washed with dilute HCl, and dried *in vacuo* at 40°C for 12 h to give **3a** (67%), **3b** (90%), **3c** (67%), and **3d** (83%). Each dye was purified by flash chromatography on silica gel. The pure dyes had the following R_f values on silica gel with the eluent 1-butanol:EtOH:pyridine:NH_4OH (4:1:2:3): **3a** = 0·30, **3b** = 0·30; **3c** = 0·35; **3d** = 0·30. Each dye exhibited a P=O band in the IR spectrum in the range 1150–1170 cm^{-1}.

3.6 Synthesis of azo dyes from compounds 4a–4d

To 13·0 g (0·133 mol) of conc. H_2SO_4 was added 1·24 g (0·0179 mol) of solid $NaNO_2$ at 10°C with stirring. The resulting mixture was stirred cold for 10 min, and then allowed to warm to room temperature. The mixture was stirred vigorously at 70°C until all of the nitrite dissolved, and cooled once again to about 10°C. To the nitrite solution was added 3·28 g (0·0179 mol) of powdered 2,4-dinitroaniline over a 10 min period. After stirring at 10°C for an additional 20 min, the mixture was poured into 43 g of ice, stirred for 10 min, and filtered. The clear filtrate was used in the coupling reaction as described above for the mononitro dyes **3**. The yields of the dyes were: **4a**, 81%; **4b**, 92%; **4c**, 67%; and **4d**, 94%. Each of the purified dyes had R_f = 0·25 on silica gel with the eluent 1-butanol:EtOH:pyridine:NH_4OH (4:1:2:3).

3.7 Application of the dyes to the fiber

A mixture of 70 ml H_2O, 1·0 g finely powdered dye, 0·075 g H_3PO_4, and 3·0 g dicyandiamide was stirred and 29% NH_4OH was added dropwise to give pH 8·5, after which the volume was adjusted to 100 ml with H_2O. The dye solutions were applied to 5·0 g samples of 100% cotton at 100% wet-pick-up, to produce a 1% add-on once the fabric was dried (110°C for 2 min). The dyes were then thermofixed at 210°C for 1 min; and the fabrics were soaped for 30 min at 80°C, rinsed, and dried.

CONCLUSION

N,*N*-Dialkyl azo dyes which contain a phosphonic acid group in one of the pendant *N*-alkyl groups form stable (washfast) linkages to cotton fibers. Although the dyes prepared in this investigation were not lightfast, it is feasible that variations in the structure of the diazo components could lead to significant improvements. The development of coupling components containing the reactive phosphonic acid group permits the preparation of a wide range of colors in this class of reactive dye.

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