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Synthesis, Characterization and Applications of New Azo Compounds Containing Phosphonic Acid

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The azo dyes (**1-6**) containg phosphonic acid were synthesized and characterized by the analytical and spectroscopic techniques and applied to the wool with the mordant and mordantless methods without the cyanamide at lower temperatures. The mordant properties of the metal ions containing different charges were compared. From the results, the dyed fibers with Cu^{2+} and Co^{2+} showed more good results for the light and rubbing fastness than other dyeing.

Key Words: Phosphonyl-azo compounds, Phosphonate-azo complexes, Mordant, Dyeing.

INTRODUCTION

Protein fibers are natural polyamides, which have a variety of amino acids as building blocks. Amino groups or carboxylic groups exist either as terminal groups on the polymer chain or in side chains. The name of the protein in wool is keratin. Keratin contains a variety of groups that are able to combine with reactive dyes. There is plenty of evidence that reactive dyes react with the various side-chains of wool[1-5].

In the past years, there have been several publications relating to phosphonated reactive dyes for use on cellulose under acidic dyeing conditions in the presence of a cyanamide type compounds at high temperatures, to give reactive dyeings with significant fixation and dyeings fast to washing under severe conditions[6-11]. The phoshonic acid acts as a bridge between the dye and fibre, immobilizing the dye on fibre. The reaction takes place at temperatures between 180-200 ºC and requires a cyanamide catalyst which limits the application method to the technique. These dyes gave some valuable indications on the possible use of fibre-reactive dye systems not subject to the limitation caused by hydrolysis. In fact, the phosphonated reactive dyes do not hydrolyze and all the unfixed dye at the end of the dyeing process is still reactive[10,11].

In the course of the dyeing, because of felting of wool fibers at high temperature, reactive azo dyes containing phosphonic acid group are not applied to wool at low pH. Dyeing of wool fiber is also not became in alkaline medium due to decomposition

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of protein structure of wool. In an acidic dyebath, the phosphonic groups in the dye become negatively charged and, since the wool is positively charged, salt linksages are formed between the dye and fibre. In the application of the dyes, different techniques of mordanting and post-treatment were used to improve colour fastness properties[12]. It is well known that the introduction of metal ion into a dye molecule improves the fastness properties of the dye, especially its fastness to light and washing fastness[13].

In the study, the final conclusion focus on dyes, which must be understood as an indicator for a distinct need for research to overcome these problems. One of the most important points that must be considered in dye design is the solubility of dye in common solvents. The most important solvent used in this industry is water due to its abundance, low cost and environment-friendliness[14]. In this sense, the new reactive azo dyes containing phosphonic acid (**1-6**) that soluble in water were synthesized and characterized by analytical and spectroscopic methods. No decomposing structure of protein fabric and subject to hydrolysis, while these dyes are directly interaction with ionic character to wool in the mordantless media. They are linked to wool by metal ions (mordant) with a coordinate-covalent bond in one-step mordation. Moreover, fastness to light, washing and rubbing of the dyed fibers were measured and discussed. All colour codes of the dyed fibers were determined from Farbenatlas[15].

EXPERIMENTAL

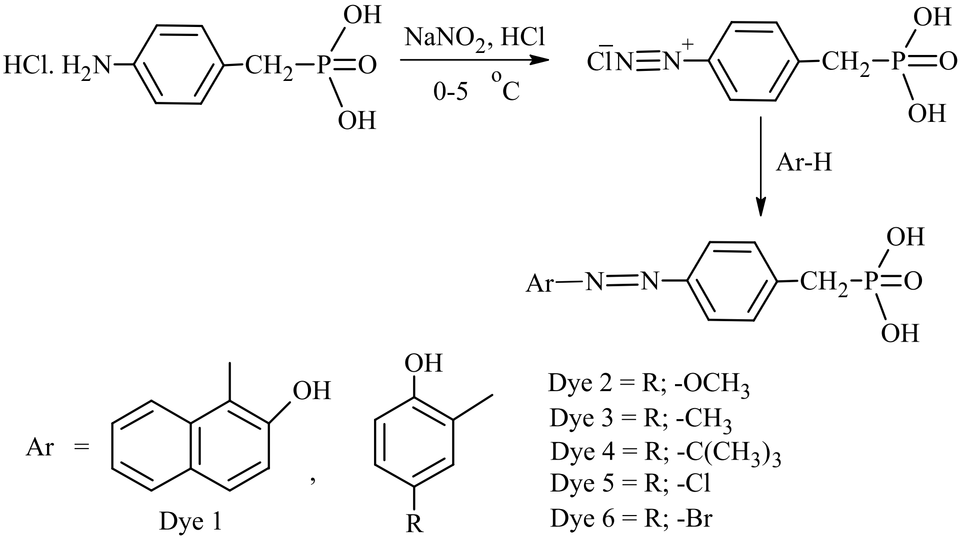
All the reagents were purchased from Merck and Aldrich and used without further purification. Melting points were determined on a Electrothermal 9200, melting point apparatus. Infrared spectra (in KBr pellets) were recorded on a Shimadzu FTIR 8300 series spectrometer. ^{1}H NMR and ^{31}P NMR spectra were obtained with a Bruker Avence DPX-400 DMSO-d_6 using TMS as an internal reference for ^{1}H NMR and 85 % H_3PO_4 as an external reference for ^{31}P NMR. The electronic spectra of the ligands were recorded with a Perkin-Elmer Lambda 45 spectrophotometer in H_2O. Mass spectra were recorded on an Agilent 1100 MSD LC/MS spectrometer. All dyeing were done in an dyeing apparatus. The light fastness was determined using artificial illumination with Xenon light according to DIN EN ISO 105 B02 (Xenotest 150F, Heraeus D-Hanay, Rudolf Chemie, Germany) and was related to the standard scale of blue dyeings. Rubbing and washing fastness were determined using standard methods of the ISO 105-X12 and ISO 105 CO6 A2S, respectively.

Synthesis of the compound (A): The compound (**A**) was synthesized according to the literature method[16]. Diethyl-4-aminobenzylphosphonate (6 g, 0.025 mol) was dissolved in HCl (60 mL, 37 %) and the resulting acidic solution was stirred at reflux for 3 h. Then, the expected product $HCl.NH_2\text{-}C_6H_4\text{-}CH_2\text{-}PO_3H_2$ (**A**) was recovered after evaporation of the solution under vacuum and triturating the solid with CH_3CN and $(C_2H_5)_2O$. Yield: 5.30 g, 96 %. mp. (dec.) 335 ºC. Anal. calc. for $C_7H_{10}NO_3P.HCl$:

C, 37.60, H, 4.96, N, 6.26. Found: C, 37.65, H, 4.98, N, 6.31. MS, m/z (positive ion): 188 $[M+H]^+$. ^{1}H NMR (δ, ppm): 8.90 (br, $-NH_2$ and $-PO_3H_2$), 7.26-7.33 (m, 4H, Ar-H), 2.98 (d, 2H, $^2J_{P-H}$ = 21.4 Hz, $-CH_2-P$), ^{31}P NMR: δ = 20.73 ppm. IR (KBr, cm^{-1}): 3413, 1265 and 1207 (P=O), 1157 and 1076 (P-OH).

Synthesis of the dyes 1-6

Diazonium salt solutions: In a 250 mL beaker, a cold solution of 1.8 g (0.025 mol) sodium nitrite in 25 mL of water was added to 5.6 g (0.025 mol) of the compound (**A**) dissolved in 50 mL NaOH (4 %) at 0-5 ºC. The solution was maintained at this temperature. 21 mL (37 % v/v) HCl was slowly added to this solution while being stirring. The end-point of the solution was checked by freshly prepared KI-starch reagent. The resulting diazonium salt solution was then stirred at 0-5 ºC for 20 min and immediately used in the following diazo coupling steps (**Scheme-I**).



Scheme-I

Coupling components: All diazo coupling reactions were done by using similar method. In the method, the diazo solution was added; to solutions of phenol compounds (β-naphthol, *p*-methoxy phenol, *p*-cresol, *p*-*t*-butyl phenol, *p*-chloro phenol and *p*-bromophenol), 0.025 mol dissolved in a solution of NaOH in water (50 mL) for 15 min, while maintaining pH at 7-8 and cooled in an ice-bath. The reaction mixture was stirred at 0-5 ºC for 2 h. The resulting dyes (**1-6**) were then acidified with conc. HCl (15 mL, 37 %). The product was filtered and washed with H_2O, CH_3CN and $(C_2H_5)_2O$, respectively. Finally it was re-crystallized from methanol. The purified dyes were dried in an oven at 50 ºC. **Scheme-I** summarizes these reactions.

Dye 1: Yield: 93 %, m.p. 270 ºC. Anal. calcd. for $C_{17}H_{15}N_2O_4P$: C, 59.65, H, 4.42, N, 8.18. Found: C, 59.60, H, 4.40, N, 8.18. MS, m/z (positive ion): 343 $[M+H]^+$. ^{1}H NMR (δ, ppm): 15.57 (s, 1H, -O---HN-N=), 6.41-8.26 (m, Ar-H), 4.39 (br, $-PO_3H_2$), 3.04 (d, 2H, $^2J_{P\text{-}H}$ = 20.7 Hz, $-CH_2$-P), ^{31}P NMR: δ = 20.49 ppm. IR (KBr, ν_{max}, cm^{-1}): 3433, 1651(-N=N-), 1261 and 1205 (P=O), 1137 and 1060 (P-OH). UV-Vis (λ_{max}, nm): 498, 414, 316, 231.

Dye 2: Yield: 87 %, m.p. 208 ºC. Anal. calcd. for $C_{14}H_{15}N_2O_5P$: C, 52.18, H, 4.69, N, 8.69. Found: C, 52.21, H, 4.70, N, 8.73. MS, m/z (positive ion): 323 $[M+H]^+$. ^{1}H NMR (δ, ppm): 10.50 (s, 1H, -OH), 6.98-8.19 (m, Ar-H), 3.75 (s, $-OCH_3$), 3.50 (br, $-PO_3H_2$), 3.04 (d, 2H, $^2J_{P\text{-}H}$ = 21.3 Hz, $-CH_2$-P), ^{31}P NMR: δ = 20.08 ppm. IR (KBr, ν_{max}, cm^{-1}): 3437, 1650 (-N=N-), 1267 and 1207 (P=O), 1149 and 1082 (P-OH). UV-Vis (λ_{max}, nm): 403, 335, 246.

Dye 3: Yield: 91 %, m.p. 233 ºC. Anal. calcd. for $C_{14}H_{15}N_2O_4P$: C, 54.91, H, 4.94, N, 9.15. Found: C, 54.91, H, 4.92, N, 9.12. MS, m/z (positive ion): 307 $[M+H]^+$. ^{1}H NMR (δ, ppm): 10.5 (s, 1H, -OH), 6.95-7.90 (m, Ar-H), 5.80 (br, $-PO_3H_2$), 3.06 (d, 2H, $^2J_{P\text{-}H}$ = 21.8 Hz, $-CH_2$-P), ^{31}P NMR: δ = 20.26 ppm. IR (KBr, ν_{max}, cm^{-1}): 3446, 1649 (-N=N-), 1278 and 1247 (P=O), 1112 and 1053 (P-OH). UV-Vis (λ_{max}, nm): 402, 337, 245.

Dye 4: Yield: 90 %, m.p. 326 ºC. Anal. calcd. for $C_{17}H_{21}N_2O_4P$: C, 58.62, H, 6.08, N, 8.04. Found: C, 58.57, H, 6.08, N, 8.10. MS, m/z (positive ion): 349 $[M+H]^+$. ^{1}H NMR (δ, ppm): 10.5 (s, 1H, -OH), 6.96-7.92 (m, Ar-H), 3.60 (br, $-PO_3H_2$), 2.80 (d, 2H, $^2J_{P\text{-}H}$ = 21.5 Hz, $-CH_2$-P), 1.30 (s, $-C(CH_3)_3$), ^{31}P NMR: δ = 20.03 ppm. IR (KBr, ν_{max}, cm^{-1}): 3409, 1649 (-N=N-), 1261 and 1170 (P=O), 1124 and 1043 (P-OH). UV-Vis (λ_{max}, nm): 403, 337, 243.

Dye 5: Yield: 76 %, m.p. 166 ºC. Anal. calcd. for $C_{13}H_{12}ClN_2O_4P$: C, 47.80, H, 3.70, N, 8.58. Found: C, 47.75, H, 3.82, N, 8.50. MS, m/z (positive ion): 327 $[M+H]^{+1}$. H-NMR (δ, ppm): 6.98-8.19 (m, Ar-H), 4.50 (br, $-PO_3H_2$), 3.04 (d, 2H, $^2J_{P\text{-}H}$ = 20.7 Hz, $-CH_2$-P), ^{31}P NMR: δ = 13.50 ppm. IR (KBr, ν_{max}, cm^{-1}): 3413, 1649 (-N=N-), 1234 (P=O), 1159 (P-OH). UV-Vis (λ_{max}, nm): 445, 346, 243

Dye 6: Yield: 75 %, m.p. 145 ºC. Anal. calcd. for $C_{13}H_{22}BrN_2O_4P$: C, 42.07, H, 3.26, N, 7.55. Found: C, 42.10, H, 3.30, N, 7.50. MS, m/z (positive ion): 372 $[M+H]^{+1}$. ^{1}H NMR (δ, ppm): 6.96-8.15 (m, Ar-H), 4.40 (br, $-PO_3H_2$), 3.05 (d, 2H, $^2\mathrm{J}_{P\text{-}H}$ = 20.6 Hz, $-CH_2$-P), ^{31}P NMR: δ = 13.50 ppm. IR (KBr, ν_{max}, cm^{-1}): 3416, 1649 (-N=N-), 1234 (P=O), 1141 (P-OH). UV-Vis (λ_{max}, nm): 437, 385, 244.

Dyeing of wool

Dyeing without mordant: The dyeing experiments were performed as a batch treatment in an Erlenmeyer flask according to the temperature-time dyeing diagram given in Fig. 1a. First the dyestuff (0.05 g) and $NaHCO_3$ (0.1 g) were dissolved in water (5 mL) in the dyebath at pH = 4-5. Wool (0.5 g) was dyed with the water solubilized the dyes (**1-6**) at 2 % owf (on weight of fabric) and a liquor ratio of 1:20 (for 1 g of wool in a dyebath volume of 20 mL is applied). Dyeing was commensed at 20 ºC and after 10 min the temperature was raised to 95 ºC over 20 min and held

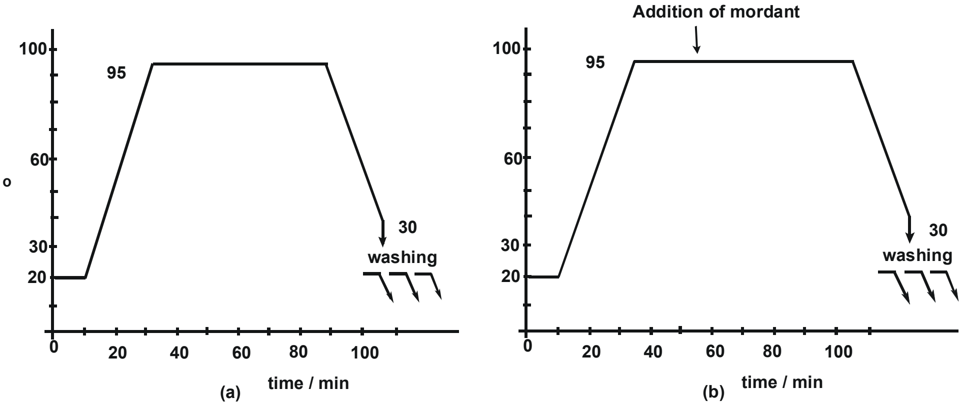


Fig. 1. Temperature-time diagram of the dyeing of the wool without mordant (a) and with mordant (b)

at this temperature for 1 h. Then dye adsorbs on the wool and finally is fixed. The dyebath was allowed to cool to 30 ºC. The dyed wool was removed, rinsed in water (5 min, room temperature) and dried at room temperature.

Dyeing together with mordant: The dyeing was designed one-bath dyeing step with direct addition of the mordant in the dyebath and carried out as a batch treatment in an Erlenmeyer flask according to the temperature-time dyeing diagram given in Fig. 1b. First the dyestuff (0.05 g) was dissolved in water (5 mL) in the dyebath adjusting with $NaHCO_3$ at pH = 4-5. Wool (0.5 g) was dyed with the water solubilized the dyes (**1-6**) at 2 % owf (on weight of fabric) and a liquor ratio of 1:20. Dyeing was commensed at 20 ºC and after 10 min of wetting, the temperature was raised to 95 ºC within 20 min. After a dyeing time of 15 min at 95 ºC the mordant was added to the dyebath. $FeCl_3·6H_2O$, $Al_2(SO_4)_3·18H_2O$, $KCr(SO_4)_2·12H_2O$, $CuSO_4·5H_2O$ and $CoSO_4·7H_2O$ were used as mordant amount of equivalent to each metal ion. The dyebath was held 95 ºC for 100 min. Finally dyes were fixed by formation of a metal complex on wool. After dyeing, the unfixed dyestuff was removed by rinsing three times with cool water (5 min, room temperature). The dyed wool was finally air dried.

Determination of fastness

Fastness to rubbing and wet treatments: Rubbing fastness of the dyed wool was evaluated using a standard procedure according to ISO 105-X12. The wash-fastness was determinated according to ISO 105-C01. The samples were treated for 0.5 h at 30 ºC. After rinsing and drying, the change in colour of sample and bleeding to white fabric (wool) was determined. The change in shade and staining of adjacent undyed fabrics were assessed using the standard grey scale (marks 1-5, 1 = poor, 5 = excellent). The results obtained are given in Table-1.

TABLE-1
MORDANT, COLOUR CODE, LIGHT, WASHING AND RUBBING FASTNESS OF DYES (**1-6**)

Dye	Mordant	Color code	Light fastness*	Washing fastness**	Rubbing fastness**	
					Wet	Dry
1	Mordantless	$Y_{20}M_{40}C_{00}$	2-3	3	4	3-4
	$KCr(SO_4)_2$	$Y_{99}M_{80}C_{00}$	3	3-4	3	4
	$Al_2(SO_4)_3$	$Y_{99}M_{70}C_{00}$	3	3-4	3	4
	$FeCl_3$	$Y_{99}M_{60}C_{00}$	3	3-4	4	4
	$CuSO_4.5H_2O$	$Y_{50}M_{99}C_{50}$	4-5	5	4-5	4-5
	$CoSO_4.6H_2O$	$Y_{40}M_{40}C_{20}$	4-5	5	4-5	4-5
2	Mordantless	$Y_{60}M_{40}C_{00}$	3-4	3	3	3-4
	$KCr(SO_4)_2$	$Y_{99}M_{40}C_{00}$	4-5	4	3-4	4
	$Al_2(SO_4)_3$	$Y_{99}M_{30}C_{00}$	4-5	4	3	4
	$FeCl_3$	$Y_{99}M_{50}C_{00}$	4-5	4	4	4
	$CuSO_4.5H_2O$	$Y_{50}M_{50}C_{30}$	5	5	4-5	4-5
	$CoSO_4.6H_2O$	$Y_{50}M_{40}C_{20}$	5	5	4-5	4-5
3	Mordantless	$Y_{50}M_{00}C_{00}$	3-4	3	3	3-4
	$KCr(SO_4)_2$	$Y_{60}M_{20}C_{00}$	4-5	4	3-4	4
	$Al_2(SO_4)_3$	$Y_{70}M_{00}C_{00}$	4-5	4	3	4
	$FeCl_3$	$Y_{60}M_{10}C_{00}$	4-5	4	4	4
	$CuSO_4.5H_2O$	$Y_{50}M_{50}C_{30}$	5	5	4-5	4-5
	$CoSO_4.6H_2O$	$Y_{50}M_{40}C_{20}$	5	5	4-5	4-5
4	Mordantless	$Y_{60}M_{10}C_{00}$	3	3	3	3-4
	$KCr(SO_4)_2$	$Y_{99}M_{30}C_{00}$	3-4	4	3-4	4
	$Al_2(SO_4)_3$	$Y_{99}M_{20}C_{00}$	3-4	4	3	4
	$FeCl_3$	$Y_{80}M_{20}C_{00}$	3-4	4	4	4
	$CuSO_4.5H_2O$	$Y_{70}M_{30}C_{00}$	4	5	4-5	4-5
	$CoSO_4.6H_2O$	$Y_{70}M_{50}C_{20}$	4	5	4-5	4-5
5	Mordantless	$Y_{99}M_{30}C_{00}$	3-4	3-4	3-4	3-4
	$KCr(SO_4)_2$	$Y_{99}M_{30}C_{10}$	4-5	4-5	4	4
	$Al_2(SO_4)_3$	$Y_{99}M_{20}C_{00}$	4-5	4-5	4	4
	$FeCl_3$	$Y_{99}M_{20}C_{10}$	4-5	4-5	4	4
	$CuSO_4.5H_2O$	$Y_{60}M_{50}C_{30}$	5	5	4-5	4-5
	$CoSO_4.6H_2O$	$Y_{60}M_{50}C_{30}$	5	5	4-5	4-5
6	Mordantless	$Y_{99}M_{30}C_{00}$	3-4	3	3	3
	$KCr(SO_4)_2$	$Y_{99}M_{30}C_{00}$	4-5	4-5	4	4
	$Al_2(SO_4)_3$	$Y_{99}M_{40}C_{00}$	4-5	4-5	4	4
	$FeCl_3$	$Y_{99}M_{50}C_{00}$	4-5	4-5	4	4
	$CuSO_4.5H_2O$	$Y_{99}M_{50}C_{70}$	5	5	4-5	4-5
	$CoSO_4.6H_2O$	$Y_{70}M_{70}C_{70}$	5	5	4-5	4-5

*In 8-grade scale; 1, the lowest; 8, the highest light fastness.

**In 5-grade scale; 1, the lowest; 5, the highest fastness.

Fastness to light: Fastness to light of dyed wool was performed according to ISO 105-B02, using a Xenotest 150F (Heraus-Hanau) apparatus. Colour change was estimated against the standard scale of blue dyeings (marks 1-8, 1 = poor, 8 = excellent). The results obtained are given in Table-1.

RESULTS AND DISCUSSION

Spectroscopic characterization

Compound (A): In order to remove the ethyl groups on the phosphonate group, the diethyl 4-aminobenzyl phosphonate in acidic media was hydrolyzed. The starting material (**A**) containing $-PO_3H_2$ group was prepared. The $-NH_2$ group of the compound (**A**) converts to the $-NH_2.HCl$[16]. This compound solubles in water and stable at room temperature without decomposition. This property is an important factor in dyeing. The compound (**A**) characterized by analytical and spectroscopic methods. Analytical data are in good agreement with the proposed structure and given in the experimental section.

In the ^1H NMR spectrum of the (**A**), the broad signal at 8.90 ppm may be assigned to the hydrogen atoms of OH groups on the $-PO_3H_2$. Broading of this signal may be due to the inter-moleculer hydrojen bonding and also IR spectrum confirms this situation. This signal disappears by adding of D_2O. The aromatic ring protons are seen at 7.26-7.33 ppm range as multiplet. The $-CH_2-$ protons are observed at 2.98 ppm as dublet[17,18]. In the ^{31}P NMR spectrum, the ^{31}P atom is seen at 20.73 ppm as singlet[19].

In the IR spectrum of the compound (**A**), the broad band at 3413 cm^{-1} can be assigned to the $\nu(OH)$ and $\nu(NH_2)$ vibrations. Band at 2860 cm^{-1} can be attributed to the benzylic $\nu(CH_2)$ vibration. The characteristic band for the free $-NH_2$ group is not observed, since the $-NH_2$ group of the compound (**A**) is in the $-NH_2.HCl$ form. The inter-molecular hydrogen bonding is shown at 2611 cm^{-1} as broad band[20]. The vibrations at 1265 and 1076 cm^{-1} range due to the $\nu(P=O)$ and $\nu(P-OH)$, respectively[20,21].

Mass spectral data of the compound (A) are given in the experimental section. The mass spectrum shows molecular ion peak at m/z 188.0 $[M+1]^+$. The compound (**A**) shows a formation of fragment ions. These peaks are found at 79.1 m/z $[H_2C = {}^+P(OH)_2]$; 105.1 m/z $[H_2N\text{-}Ph\text{-}{}^+CH_2]$.

The diazotized compound (**A**) is coupled to phenols such as β-naphthol, *p*-methoxy phenol, *p*-cresol, *p*-*t*-butyl phenol, *p*-chloro phenol and *p*-bromo phenol. The dyes 4-[(β-hydroxy)-α-naphthylazo]benzylphosphonic acid (**1**), 4-[(2-hydroxy-5-methoxy)-phenylazo]benzylphosphonic acid (**2**), 4-[(2-hydroxy-5-methyl)phenyl-azo]benzyl-phosphonic acid (**3**), 4-[(2-hydroxy-5-*t*-butyl)phenylazo]benzyl-phosphonic acid (**4**), 4-[(2-hydroxy-5-chloro)phenylazo]benzylphosphonic acid (**5**) and 4-[(2-hydroxy-5-bromo)phenylazo]benzylphosphonic acid (**6**) were synthesized. The proposed structure of the synthesized compounds are given in **Scheme-I**.

The dyes (**1-6**) soluble in polar solvents such as H_2O, EtOH, MeOH and DMSO, but insoluble in apolar solvents such as hexane, heptane or toluene. All dyes are very stable at room temperature without decomposition and obtained in high yields at pH = 2-3 values.

The $^1H(^{31}P)$ NMR spectral data of the dyes (**1-6**) are given in the experimental section. In the ^1H NMR spectra of the dyes, whereas the OH peak of the dye (**1**) is shown at 15.07 ppm as a singlet, for the dyes (**2-4**) are shown in the 10.05-10.50 ppm range[22]. In the dyes (**1-6**), multiplet in the 6.41-8.26 ppm range and dublet in the 2.80-3.06 ppm range are attributed to the aromatic and $-CH_2-P$ protons[17,18], respectively. There is not individual region for the protons of the $-P(O)(OH)_2$ group. In the spectrum of the dye (**1**), this group is shown as a broad band at 8.90 ppm. In like manner, in the spectrum of the dye (**3**), the broad singlet at 3.50 ppm can be attributed to same group. These broad bands due to the intermolecular hydrogen bonding disapper upon addition of D_2O. A singlets at 1.30 ppm for $-C(CH_3)_3$ in the dye (**5**), at 2.30 ppm for $-CH_3$ in the dye (**4**) and at 3.75 ppm for $-OCH_3$ in the dye (**3**) have been observed[17]. The ^{31}P NMR spectra of all dyes, the signal in the range 20.73-13.50 ppm can be attributed to the phosphorous atom[19]. In the ^{31}P NMR spectra of dyes (**5**) and (**6**), this signal shifts to the lower regions than other dyes. This situation may be explain by the electron-withdrawing properties of the Cl and Br atoms with inductive effect.

The FT-IR spectral data of all the dyes are given in the experimental section. In the FT-IR spectra of the dyes (**1-6**), the broad bands in the 3446-3413 cm^{-1} range can be attributed to the ν(OH) vibration. Moreover, the dyes have the azo (-N=N-) group and this group is observed in the 1650-1649 cm^{-1} range[23,24]. The bands in the 1278-1170 cm^{-1} and 1159-1043 cm^{-1} ranges may be assigned to the ν(P=O) and ν(P-OH) vibrations, respectively[20,21].

The UV spectra of the dyes (**1-6**) are studied in water and the obtained data are given in the experimental section. The dyes (**2-4**) show the similar electronic properties. The bands at 402 and 403 nm can be attributed to the $n-\pi^*$ transitions. However, the dyes (**5**) and (**6**) show the similar properties. In these dyes, the $n-\pi^*$ transition is seen at 445 and 437 nm. The dye (**1**) shows the same transition at 498 nm. The differences may be due to the electronic properties of the dyes. The bands in the 385-231 nm range are assigned to the $\pi-\pi^*$ and $\delta-\pi^*$ transitions.

Mass spectra of the dyes (**1-6**) show signals at 343.0 m/z and 344.0 m/z for dye (**1**), at 323.0 m/z and 324.0 m/z for the dye (**2**), at 307.0 m/z and 308.0 m/z for the dye (**3**), at 349.0 m/z and 350.0 m/z for the dye (**4**), at 327.0 m/z and 328.0 m/z for the dye (**5**) and at 372.0 m/z and 373.0 m/z for the dye (**6**) corresponding to their $[M+1]^+$ and $[M+2]^{2+}$ ion peaks, respectively. All dyes show similar formation of fragment ions: (i) cleavege at the C-P bond, $(-CH_2-PO_3H_2)$, (ii) cleavege at the azo bond or adjant to the azo bond.

Dyeing process: A general dyeing method was used for all investigated dyes without significant changes. The dyeings were performed on wool (protein fiber) to get information about the influence of substrate on colour depth, shade and fastness properties. Since all the dyes contain -PO_3H_2 group is soluble in water, the dyeing processes were applied to wool in water solution. The dyeings were done both in mordantless and mordant media. The first dyeing procedure was independent of mordant. In this dyeing, the samples were immersed into the dyebath containing the dyestuff. There are directly ionic interactions among the wool (due to amine groups) and polar edges of the dyes in the dyeing without mordant.

In the second type of dyeing, while the samples were immersed into the dyebath, mordants were added to the dyebath. Various metal ions such as Cu^{2+}, Co^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+} were used as a mordant. In the dyeing with mordant, the donor atoms such as nitrogen and oxygen of the wool coordinate to the metal ions[24]. As a different from the ionic-interaction in the dyeing with mordant, the coordinate-covalent bond forms. Therefore, the colours of the dyed wool with mordant are more intense than with mordantless. The direct addition of the mordant into the dyebath might cause losses of dyestuff due to partial precipitation of dyestuff, but such a proceeding forms the basis for a one-bath dyeing process. From the point of dyestuff consumption, a two-bath process seems favourable. For a dyehouse, the use of separated baths for mordanting and dyeing is undesirable with regard to time of dyeing, further treatment, or recycling of the mordanting baths. The proposed introduction of a one-bath procedure can thus be understood as a technical compromise required to implement the technology into a modern dyehouse[12].

All the dyed wool were examined for fastness properties. To illustrate the range of colour achived, coordinates of the different dyeings and description of the shades are shown in Table-1. The fastness values of dyed fibers to light (blue scale), washing and rubbing (grey scale) are given in Table-1. As they can be seen from the data, the fibers dyed without mordant showed poor light fastness, good rubbing/washing fastness[11] and the use of mordant had good light/washing and very good rubbing fastness. Metallized azo dye compounds enhanced lightfastness arising from protection of the azo bond through back bonding, which utilize the empty *d*-orbitals of the transition metals[14,25]. Moreover, the dyed fibers with Cu^{2+} and Co^{2+} showed good results for the light and rubbing fastness than the metal free dyes. But, the wool which dyed with Al^{3+}, Cr^{3+} and Fe^{3+} exhibited poor light fastness than the Cu^{2+} and Co^{2+}. The presence of the bromo or chloro atom at the 4-position of the phenolic rings of the dyes (**5**) and (**6**) has much effect on the fastness properties of the dyes. While the colours of the dyed wool with dyes (**5**) and (**6**) are bright, the other wool fibers are dull. As seen from Table-1, the colour codes of the dyed fibers were determined from Farbenatlas (Y; Yellow; M; Red, C; Cyan blue)[15].

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