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Novel 2-phenyl-3-{4'-[*N*-(4"-aminophenyl)carbamoyl]-phenyl}--quinazoline-4(3*H*)one-6-sulphonic acid based mono azo reactive dyes

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Abstract: A series of new heterocyclic mono azo reactive dyes **7a**–**m** were prepared by diazotization of 2-phenyl-3-{4'-[*N*-(4"-aminophenyl)carbamoyl]-phenyl}-quinazoline-4(3*H*)-one-6-sulphonic acid (**3**) and coupling with various cyanurated coupling components **6a**–**m** and their dyeing performance on silk, wool and cotton fibres was assessed. These dyes were found to give a variety of colour shades with very good depth and levelness on the fibres. All the compounds were identified by conventional method (IR and ^{1}H-NMR) and elemental analyses. The percentage dye bath exhaustion on different fibres was reasonably good and acceptable. The dyed fibre showed moderate to very good fastness to light, washing and rubbing.

Keyword: quinazoline-4(3*H*)-one; mono azo reactive dyes; dyeing; fastness properties.

INTRODUCTION

In recent years, the development of new structures of reactive dyes has been a subject of interest and many novel structures useful in commercial application to silk, wool and cotton, as well as their blends with other fibres, have been discovered. The utility of quinazoline derivatives for the production of some commercial dyes and pigment, both for natural and man-made fibre, is known.[1,2] Intensive efforts have been made in the investigation of mono azo dyes containing a heterocyclic moiety, such as amino quinazoline,[3] as the diazo component owing to the marked bathochromic effect of such groups compared to the corresponding benzoid compound.[4]

In view of encouraging reports about the technical applications of the dyes based on the 4-oxoquinazoline system,[5,6] it was considered of interest to under-

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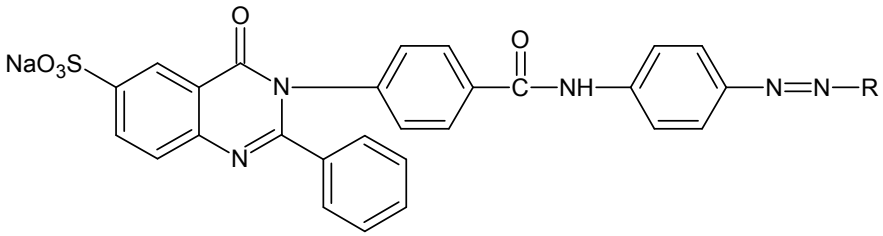
take the synthesis and study of the dyeing properties of azo dyes based on 2-styryl-3-(2'-chlorophenyl)-6-amino-4-oxoquinazoline.

In the present investigation, the synthetic pathway to 2-phenyl-3-{4'-[*N*-(4"--aminophenyl)carbamoyl]-phenyl}-quinazoline-4(3*H*)-one-6-sulphonic acid (**3**) from a readily available starting material, *i.e.*, 5-sulpho anthranilic acid, was examined. The effect of the presence of the $–SO_3Na$ and –CONH–groups in the quinazoline-based structure of the reactive dyes was studied in relation to the colour and dyeing properties of the heterocyclic reactive dyes **7a**–**m**.

The general structure of the reactive dyes **7a**–**m** is:



where R = various 4-nitroanilino cyanurated coupling components (**6a**–**m**).

RESULTS AND DISCUSSION

Chemistry

The new series of reactive dyes **7a**–**m** containing the quinazolinone and benzanilide moieties were synthesized by condensation of benzoxazine derivative **1** and the diaminobenzanilide moiety **3**. This condensed product on diazotization and coupling with various 4-nitroanililno cyanurated coupling components **6a**–**m** produced a novel series of heterocyclic reactive dyes. These series of dyes have found wide application in the dyeing of wool, silk and cotton fibres. The presence of quinazolinone structure in the dye molecule results in excellent dyeing properties, including low sublimation and high thermal stability.

Characterization of the isolated intermediates and dyes

*2-Phenyl-4-oxo-3,1-benzoxazine-6-suphonic acid (**1**)*. Yield 85 %; m.p. 107 °C; Anal. Calcd. for $C_{14}H_9O_5NS$: C, 55.44; H, 2.99; N, 4.62 %. Found: C, 55.40; H, 2.95; N, 4.60 %. IR (KBr, cm^{-1}) 1750 (C=O stretching of benzoxazine), 1380 (C–N stretching of benzoxazine), 1042 (S=O stretching of sulphonic acid group). ^{1}H NMR (300 MHz, DMSO-d_6, δ / ppm): 11.2 (1H, *s*, SO_3H), 6.72–8.05 (8H, *m*, Ar–H).

*4,4'-Diaminobenzanilide (**2**)*. Yield 75 %; m.p. 205 °C; Anal. Calcd. for $C_{13}H_{13}ON_3$: C, 68.70; H, 5.77; N, 18.49 %. Found: C, 68.65; H, 5.72; N, 18.44 %. IR (KBr, cm^{-1}) 1695 (C=O stretching of amide group), 3325, 2985 (N–H stretching (asym. and sym.) of amide group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 8.62 (1H, *s*, –CONH), 5.74 (4H, *s*, 2 $–NH_2$), 6.72–8.25 (8H, *m*, Ar–H).

*2-Phenyl-3{4'-[N-(4"-aminophenyl)carbamoyl]-phenyl}-quinazoline-4-(3*H*)--one-6-sulphonic acid (**3**)*. Yield 75 %, m. p. 193 °C. Anal. Calcd. for $C_{27}H_{20}O_5N_4S_1$: C, 63.27; H, 3.93; N, 10.93 %. Found: C, 63.92; H, 3.88; N, 10.90 %. IR (KBr, cm^{-1}): 3515 (N–H stretching of primary $–NH_2$ group), 1675 (C=O stretching of quinazolinone), 1395 (C–N stretching of quinazoline structure), 1040 (S=O stretching of $–SO_3H$ group), 3415, 2995 (asym. and sym. N–H stretching of amide). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm) 5.78 (2H, *s*, $–NH_2$), 8.64 (1H, *s*, –CONH), 11.6 (1H, *s*, $–SO_3H$), 6.78–8.15 (16H, *m*, Ar–H).

*Sodium 5-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-4-hydroxy-3-((4-(imino(4-(4-oxo-2-phenyl-6-sulfonatoquinazolin-3(4*H*)-yl)phenyl)methoxy)phenyl)diazenyl)naphthalene-2,7-disulfonate (**7a**)*. Yield: 85 %; Anal. Calcd. for $C_{46}H_{27}O_{14}N_{11}ClS_3Na_3$: C, 47.69; H, 2.35; N, 13.30. Found: C, 47.63; H, 2.31; N, 13.28 %. IR (KBr, cm^{-1}): 3360–3680 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1660 (C=O stretching of quinazoline ring), 1430 (N=N stretching of azo group), 1382 (C–N), 1360, 1112, 1049 (S=O stretching of sulphonates), 1501, 1308 (N=O asym. and sym. stretching of nitro group), 762 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.32 (1H, *s*, –OH), 4.16 (2H, *s*, 2 –NH), 8.65 (1H, *s*, –CONH), 6.82–7.95 (23H, *m*, Ar–H).

*Sodium 3-(4-((4-((7-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo-2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7b**)*. Yield: 83 %; Anal. Calcd. for $C_{46}H_{28}O_{11}N_{11}ClS_2Na_2$: C, 52.30; H, 2.67; N, 14.58 %. Found: C, 52.26; H, 2.63; N, 14.55 %, IR (KBr, cm^{-1}): 3360–3680 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1662 (C=O stretching of quinazoline ring), 1425 (N=N stretching of azo group), 1380 (C–N), 1360, 1115, 1055 (S=O stretching of sulphonates), 1510, 1310 (N=O asym. and sym. stretching of nitro group), 765 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.35 (1H, *s*, –OH), 4.12 (2H, *s*, 2 –NH), 8.62 (1H, *s*, –CONH), 6.81–7.90 (24H, *m*, Ar–H).

*Sodium 3-(4-((4-((6-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo-2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7c**)*. Yield: 78 %; Anal. Calcd. For $C_{46}H_{28}O_{11}N_{11}ClS_2Na_2$: C, 52.30; H, 2.67; N, 14.58 %. Found: C, 52.25; H, 2.62; N, 14.56 5. IR (KBr, cm^{-1}): 3350–3700 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1656 (C=O stretching of quinazoline ring), 1420 (N=N stretching of azo group), 1385 (C–N), 1340, 1110, 1045 (S=O stretching of sulphonates), 1505, 1315 (N=O asym. and sym. stretching of nitro group), 760 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.38 (1H, *s*, –OH), 4.18 (2H, *s*, 2 –NH), 8.66 (1H, *s*, –CONH), 6.85–7.92 (24H, *m*, Ar–H).

Sodium 3-(4-((4-(((6-(((4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-yl)-(methyl)amino)-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl)phenoxy)(imi-

*no)methyl)phenyl)-4-oxo-2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7d**)*. Yield: 82 %; Anal. Calcd. for $C_{47}H_{30}O_{11}N_{11}ClS_2Na_2$: C, 52.74; H, 2.83; N, 14.39 %. Found: C, 52.70; H, 2.80; N, 14.36 %. IR (KBr, cm^{-1}): 3355–3690 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1670 (C=O stretching of quinazoline ring), 1435 (N=N stretching of azo group), 1380 (C–N), 1365, 1115, 1045 (S=O stretching of sulphonates), 1510, 1310 (N=O asym. and sym. stretching of nitro group), 766 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.31 (1H, *s*, –OH), 4.20 (1H, *s*, –NH), 8.57 (1H, *s*, –CONH), 8.62 (1H, *s*, –CONH), 6.86–7.92 (24H, *m*, Ar–H).

*Sodium 3-(4-((4-((6-((4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-yl)-(phenyl)amino)-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo-2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7e**)*. Yield: 84 %; Anal. Calcd. for $C_{52}H_{32}O_{11}N_{11}ClS_2Na_2$: C, 55.15; H, 2.85; N, 13.60 %. Found: C, 55.10; H, 2.81; N, 13.57 %. IR (KBr, cm^{-1}): 3360–3700 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1665 (C=O stretching of quinazoline ring), 1430 (N=N stretching of azo group), 1385 (C–N), 1370, 1110, 1040 (S=O stretching of sulphonates), 1505, 1310 (N=O asym. and sym. stretching of nitro group), 765 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.32 (1H, *s*, –OH), 4.15 (H, *s*, –NH), 8.68 (1H, *s*, –CONH), 6.78–8.05 (29H, *m*, Ar–H).

*Sodium 4-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-5-hydroxy-6-((4-(imino(4-(4-oxo-2-phenyl-6-sulfonatoquinazolin-3(4*H*)-yl)phenyl)methoxy)phenyl)diazenyl)naphthalene-1,3-disulfonate (**7f**)*. Yield: 77 %; Anal. Calcd. for $C_{46}H_{27}O_{14}N_{11}ClS_3Na_3$: C, 47.69; H, 2.37; N, 13.30 %. Found: C, 47.63; H, 2.33; N, 13.28 %. IR (KBr, cm^{-1}): 3345–3690 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1670 (C=O stretching of quinazoline ring), 1425 (N=N stretching of azo group), 1365 (C–N), 1375, 1105, 1042 (S=O stretching of sulphonates), 1510, 1315 (N=O asym. and sym. stretching of nitro group), 765 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.30 (1H, *s*, –OH), 4.12 (2H, *s*, 2 –NH), 8.65 (1H, *s*, –CONH), 6.83–7.98 (23H, *m*, Ar–H).

*Sodium 3-(4-((4-((1-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-5-sulfonatonaphthalen-2-yl)diazenyl)phenoxy(imino)methyl)phenyl)-4-oxo-2--phenyl-3,4-dihydroquinazoline-6-sulfonate (**7g**)*. Yield: 76 %; Anal. Calcd. for $C_{46}H_{28}O_{10}N_{11}ClS_2Na_2$: C, 53.11; H, 2.71; N, 14.81 %. Found: C, 53.09; H, 2.68; N, 14.78 %. IR (KBr, cm^{-1}): 3355–3705 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1662 (C=O stretching of quinazoline ring), 1430 (N=N stretching of azo group), 1372 (C–N), 1372, 1115, 1052 (S=O stretching of sulphonates), 1505, 1315 (N=O asym. and sym. stretching of nitro group), 766 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.18 (2H, *s*, 2 –NH), 8.70 (1H, *s*, –CONH), 6.75–7.93 (25H, *m*, Ar–H).

Sodium 3-(4-((4-((2-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-6-sulfonatonaphthalen-1-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo-

*2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7h**)*. Yield: 80 %; Anal. Calcd. for $C_{46}H_{28}O_{10}N_{11}ClS_2Na_2$: C, 53.11; H, 2.71; N, 14.81 %. Found: C, 53.08; H, 2.67; N, 14.77 %. IR (KBr, cm^{-1}): 3350–3715 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1665 (C=O stretching of quinazoline ring), 1435 (N=N stretching of azo group), 1380 (C–N), 1360, 1118, 1050 (S=O stretching of sulphonates), 1505, 1310 (N=O asym. and sym. stretching of nitro group), 762 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.17 (2H, *s*, 2 –NH), 8.68 (1H, *s*, –CONH), 6.82–7.98 (25H, *m*, Ar–H).

*Sodium 3-(4-((4-((2-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)naphthalene-1-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo-2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7i**)*. Yield: 82 %; Anal. Calcd. for $C_{46}H_{28}O_7N_{11}ClSNa_2$: C, 58.88; H, 3.12; N, 16.04 %. Found: C, 58.84; H, 3.09; N, 16.01 %. IR (KBr, cm^{-1}): 3350–3700 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1670 (C=O stretching of quinazoline ring), 1422 (N=N stretching of azo group), 1388 (C–N), 1365, 1120, 1060 (S=O stretching of sulphonates), 1510, 1315 (N=O asym. and sym. stretching of nitro group), 760 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6 / δ, ppm): 4.15 (2H, *s*, 2 –NH), 8.65 (1H, *s*, –CONH), 6.86–7.95 (26H, *m*, Ar–H).

*Sodium 3-(4-((4-((2-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-5-sulfonatonaphthalen-1-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo--2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7j**)*. Yield: 85 %; Anal. Calcd. for $C_{46}H_{27}O_{13}N_{11}ClS_3Na_3$: C, 48.36; H, 2.38; N, 13.49 %. Found: C, 48.32; H, 2.34; N, 13.46 %. IR (KBr, cm^{-1}): 3360–3700 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1660 (C=O stretching of quinazoline ring), 1445 (N=N stretching of azo group), 1380 (C–N), 1360, 1113, 1047 (S=O stretching of sulphonates), 1505, 1308 (N=O asym. and sym. stretching of nitro group), 765 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.14 (2H, *s*, 2 –NH), 8.61 (1H, *s*, –CONH), 6.85–7.93 (25H, *m*, Ar–H).

*Sodium 3-(4-((4-((1-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-8-sulfonatonaphthalen-2-yl)diazenyl)phenoxy)(imino)methyl)phenyl)-4-oxo--2-phenyl-3,4-dihydroquinazoline-6-sulfonate (**7k**)*. Yield: 80 %; Anal. Calcd. For $C_{46}H_{28}O_{10}N_{11}ClS_2Na_2$: C, 53.11; H, 2.71; N, 14.81 %. Found: C, 53.06; H, 2.68; N, 14.76 %. IR (KBr, cm^{-1}): 3355–3700 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1675 (C=O stretching of quinazoline ring), 1440 (N=N stretching of azo group), 1385 (C–N), 1360, 1112, 1055 (S=O stretching of sulphonates), 1511, 1307 (N=O asym. and sym. stretching of nitro group), 763 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.16 (2H, *s*, 2 –NH), 8.66 (1H, *s*, –CONH), 6.78–7.96 (25H, *m*, Ar–H).

*Sodium 8-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-7-((4--(imino(4-(4-oxo-2-phenyl-6-sulfonatoquinazolin-3(4*H*)-yl)phenyl)methoxy)phenyl)diazenyl)naphthalene-1,3,6-trisulfonate (**7l**)*. Yield: 85 %; Anal. Calcd. for

$C_{46}H_{26}O_{16}N_{11}ClS_4Na_4$: C, 44.40; H, 2.11; N, 12.38 %. Found: C, 44.36; H, 2.08; N, 12.34 %. IR (KBr, cm^{-1}): 3360–3705 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1662 (C=O stretching of quinazoline ring), 1445 (N=N stretching of azo group), 1382 (C–N), 1365, 1120, 1048 (S=O stretching of sulphonates), 1510, 1315 (N=O asym. and sym. stretching of nitro group), 766 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.18 (2H, *s*, 2 –NH), 8.62 (1H, *s*, –CONH), 6.76–7.96 (23H, *m*, Ar–H).

*Sodium 4-(4-chloro-6-(4-nitrophenylamino)-1,3,5-triazin-2-ylamino)-5-hydroxy-6-((4-(imino(4-(4-oxo-2-phenyl-6-sulfonatoquinazolin-3(4*H*)-yl)phenyl)methoxy)phenyl)diazenyl)naphthalene-1,7-disulfonate (**7m**)*. Yield: 78 %; Anal. Calcd. for $C_{46}H_{27}O_{14}N_{11}ClS_3Na_3$: C, 47.69; H, 2.35; N, 13.30 %. Found: C, 47.64; H, 2.31; N, 13.26 %. IR (KBr, cm^{-1}): 3370–3705 (O–H and N–H stretching of –OH and $–NH_2$ groups), 1665 (C=O stretching of quinazoline ring), 1445 (N=N stretching of azo group), 1380 (C–N), 1355, 1120, 1045 (S=O stretching of sulphonates), 1505, 1310 (N=O asym. and sym. stretching of nitro group), 760 (C–Cl stretching of chloro group). ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.35 (1H, *s*, –OH), 4.15 (2H, *s*, 2 –NH), 8.62 (1H, *s*, –CONH), 6.75–7.98 (23H, *m*, Ar–H).

Spectral properties

The absorption maxima (λ_{max}) and logarithm of the molar extinction coefficient (log ε) of all the prepared dyes **7a**–**m** are given in Table I. The absorption maxima of **7a**–**m** were recorded in DMF solution. The absorption maxima were in the range of 475–543 nm. The value of logarithm of molar extinction co-efficient (log ε) of the dyes **7a**–**m** were in the range 4.15–4.42, indicating their good absorption intensity.

TABLE I. Exhaustion and fixation data of the synthesised dyes **7a**–**m** (S – silk, W – wool, C – cotton)

Dye	Colour	λ_{max} / nm	log ε	Exhaustion, %			Fixation, %		
				S	W	C	S	W	C
7a	Pink	543	4.42	75.50	70.80	70.55	91.53	91.08	91.44
7b	Reddish brown	503	4.30	73.30	66.82	67.66	88.78	89.25	84.85
7c	Brown	495	4.22	70.80	70.47	69.72	85.54	92.42	85.57
7d	Orange	485	4.15	69.55	65.55	73.78	89.14	87.81	88.89
7e	Reddish brown	475	4.27	67.87	66.18	69.45	91.84	85.54	87.55
7f	Light brown	520	4.32	72.60	71.15	69.57	84.02	88.75	86.87
7g	Light orange	485	4.30	70.35	68.80	71.88	85.70	84.65	91.49
7h	Orange	480	4.15	75.45	66.27	71.52	90.12	91.81	88.78
7i	Orange	475	4.40	68.80	68.40	65.17	86.73	86.84	84.38
7j	Light yellow	490	4.25	71.23	67.23	72.60	90.45	87.45	87.58
7k	Brown	485	4.27	75.95	65.17	68.28	91.82	84.47	85.88
7l	Orange	475	4.30	69.95	69.96	70.70	90.16	89.29	86.57
7m	Greenish yellow	525	4.23	72.55	68.82	68.04	91.52	88.91	88.92

Dyeing of fibres

All the dyes (**7a**–**m**) were applied on silk, wool and cotton fabrics in 2 % shade according to the usual procedure.[7] The variation in the hues of the dyed fabric result from both the nature and position of the substituent present on the naphthalene ring. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes for the fabric.

Exhaustion and fixation study

Dye uptake by the fibre was measured by sampling the dye bath before and dyeing. The absorbance of diluted dye solution was measured at the λ_{max} of the dye. Percentage dye bath exhaustion was calculated using following relationship:

$$\text{Exhaustion (\%)} = 100\frac{\text{Initial O.D.} - \text{Final O.D.}}{\text{Initial O.D.}}$$

The percentage exhaustion[8] of 2 % dyeing on cotton ranged from 65 to 74 %, for silk fabric from 67 to 75 % and wool from 65 to 71 %. The percentage fixation[9] of 2 % dyeing on cotton fabric ranged from 84 to 91 %, for silk from 84 to 92% and for wool from 84 to 90 % (the obtained results are summarized in Table I).

Fastness properties

The light fastness of all the reactive dyes (**7a**–**m**) on silk, wool and cotton fibres is moderate to very good. The obtained result of washing fastness of the dyes for silk, wool and cotton fibres showed they are good to excellent. Fastness to rubbing (dry and wet) of the dyed pattern was moderate to very good for silk, wool and cotton fibres (Table II). These are attributed to the good penetration and affinity of the dyes for the fibres.

TABLE II. Fastness properties of the synthesised dyes **7a**–**m** (S – silk, W – wool, C – cotton; light fastness: 1 – poor, 2 – slight, 3 – moderate, 4 – fair, 5 – good, 6 – very good; wash and rubbing fastness: 1 – poor, 2 – fair, 3 – good, 4 – very good, 5 – excellent)

Dye	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
7a	5	6	4	5	4–5	4	4–5	3–4	3	3–4	4	5
7b	4	4–5	4–5	4	4	3–4	3–4	3	4	4	4	3
7c	5	5	3	5	3–4	3	4	4–5	5	3–4	6	4
7d	3	4	5	4	4	4	3–4	3	4	4	4–5	3–4
7e	4	3–4	3	3–4	3–4	5	3	5	3	3	4–5	4
7f	4–5	4	4	4–5	4	4–5	4–5	3–4	3–4	3–4	4	3–4
7g	6	4	3	3	4	3–4	4–5	4	4	3	4	4
7h	4	5	4–5	4	5	4	4	3–4	3	4	4–5	5
7i	4	5	4–5	4	4	3–4	3	3	3–4	5	3	5
7j	3–4	5	3	3–4	3	4–5	5	4	3	3	4	3
7k	4	4–5	4	5	4–5	3–4	4	4	3–4	5	4–5	4

TABLE II. Continued

Dye	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
7l	4	5	3–4	3–4	4	5	4	4–5	3	4–5	3	3–4
7m	5–6	4	5	4–5	3–4	4–5	3–4	4	3–4	4	3	4–5

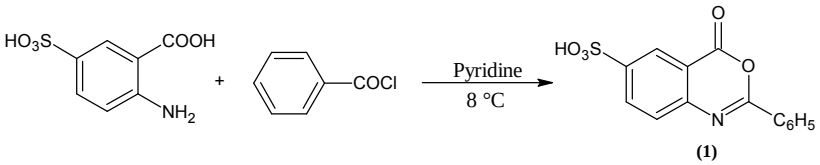
EXPERIMENTAL

General

All the melting points (m.p.) were determined in open capillaries and are uncorrected. Elemental analysis for carbon, hydrogen and nitrogen were realised on a Carlo Erba 1108 elemental analyzer. The purity of all the dyes has been checked by TLC[10] using aluminium plates coated with silica gel 60 F254 (Merck), eluent *iso*-butanol:*n*-propanol:ethyl acetate:water (2:4:1:3). The IR spectra were recorded in KBr on a Perkin-Elmer model-881 spectrophotometer and the ^{1}H-NMR spectra on a Brucker DRX-300 (300 MHz FT-NMR) instrument using TMS as the internal standard and DMSO-*d*6 as the solvent. Chemical shifts are given in δ (ppm). Absorption spectra were recorded on a Beckman DB-GT Grating spectrophotometer. The light fastness was assessed in accordance with BS: 1006-1978.[11] The rubbing fastness test was performed with a Crockmeter (Atlas) in accordance with AATCC-1961[12] and the wash fastness test in accordance with IS: 765-1979.[13]

*Preparation of 2-phenyl-4-oxo-3,1-benzoxazine-6-suphonic acid (**1**)[14]*

Benzoyl chloride (140.5 g, 1.0 mol) was added dropwise over the period of 1 h to 5-sulpho anthranilic acid (217 g, 1.0 mol) dissolved in pyridine (60 ml), under constant stirring at 8 °C. After the completion of the addition, the reaction mixture was stirred for 30 min at room temperature. At the end of the reaction, a solid mass was obtained, which was filtered, washed successively with sodium bicarbonate solution (to remove unreacted acid) and then with water, dried and recrystallized from rectified spirit. (The general route for the preparation of 2-phenyl-4-oxo-3,1-benzoxazine-6-suphonic acid (**1**) is outlined in Scheme 1).



(1)

Scheme 1. Synthetic route to 2-phenyl-4-oxo-3,1-benzoxazine-6-sulphonic acid (**1**).

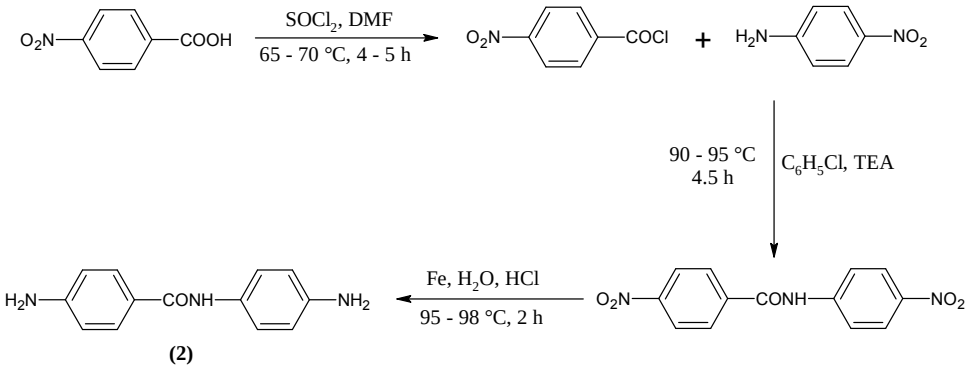
*Preparation of 4,4'-diaminobenzanilide (**2**)*

The title compound was prepared by the process described in the literature.[15] (The general route for the preparation of 4,4'-diaminobenzanilide (**2**) is outlined in Scheme 2).

*Preparation of 2-phenyl-3{4'-[*N*-(4"-aminophenyl)carbamoyl]-phenyl}-quinazoline-4-(3*H*)--one-6-sulphonic acid (**3**)[16]*

A mixture of compound **1** (0.05 mol) and **2** (0.05 mol) in dry pyridine (50 ml) was heated under reflux for 6 h under anhydrous reaction conditions and then allowed to cool to room temperature. The reaction mixture was treated with dilute HCl and stirred. A solid separate out which was filtered off and washed with water to remove any adhered pyridine. The

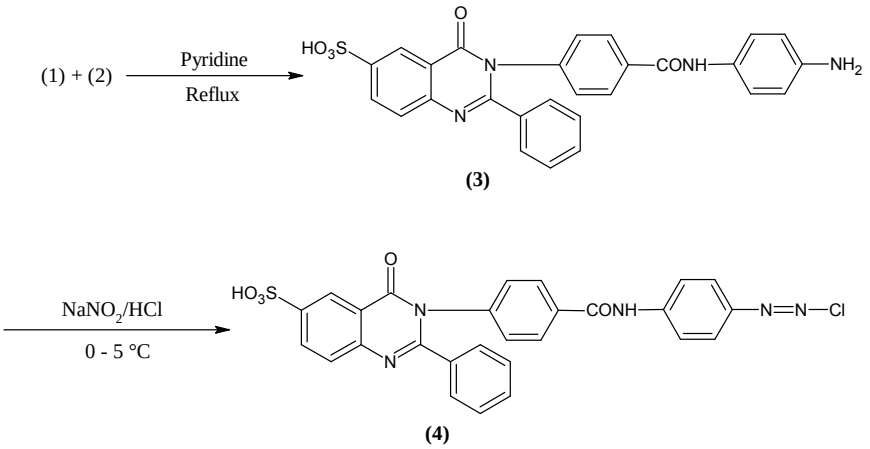
thus obtained crude quinazoline was dried under vacuum and recrystallized from 50 vol.% ethanol in water). (The general route for the preparation of compound **3** is outlined in Scheme 3).



Scheme 2. Synthetic route to the diaminobenzanilide (**2**).

*Diazotation of 2-phenyl-3{4'-[*N*-(4"-aminophenyl)carbamoyl]-phenyl}-quinazoline-4-(3*H*)--one-6-sulphonic acid (**4**)*

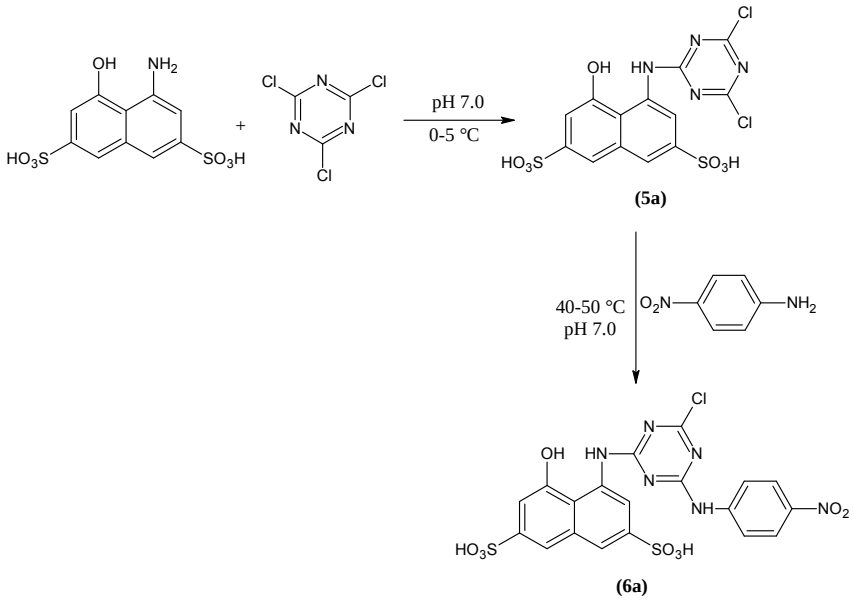
Compound **3** (2.56 g, 0.005 mol) was suspended in water (60 ml). Hydrochloric acid (0.36 g) was added dropwise to this well-stirred suspension. The mixture was gradually heated up to 70 °C until a clear solution was obtained. The solution was cooled to 0–5 °C in an ice bath. A solution of $NaNO_2$ (0.6 g) in water (4 ml) previously cooled to 0 °C was then added over a period of five minutes with stirring. The stirring was continued for 1 h, maintaining the same temperature. The excess of nitrous acid (gave a positive test on starch-iodide paper) was decomposed with the required amount of sulphamic acid. The thus obtained clear diazo solution **4** at 0–5 °C was used for the subsequent coupling reaction. (The general route for the preparation of compound **4** is outlined in Scheme 3).



Scheme 3. Synthetic route to 2-phenyl-3-{4'-[*N*-(4"-aminophenyl)carbamoyl]-phenyl}-quinazoline-4-(3*H*)-one-6-sulphonic acid (**3**) and its diazonium salt **4**.

Preparation of 4-nitro anilino cyanurated H-acid

*Cyanuration of H-acid (**5a**)*. Cyanuric chloride (1.85 g, 0.01 mol) was stirred in acetone (25 ml) at a temperature below 5 °C for a period of an hour. A neutral solution of H acid (3.19 g, 0.01mol) in aqueous sodium carbonate solution (10 % w/v) was then added in small amounts over about an hour. The pH was maintained neutral by the simultaneous addition of sodium carbonate solution (1 % w/v). The reaction mixture was stirred at 0–5 °C for further 4 h when a clear solution was obtained. (The general route for the preparation of compound **5a** is outlined in Scheme 4). The resultant solution was used for the condensation reaction with 4-nitro aniline.



Scheme 4. Synthetic route to the cyanurated H-acid **5** and 4-nitro anilinocyanurated H-acid **6a**.

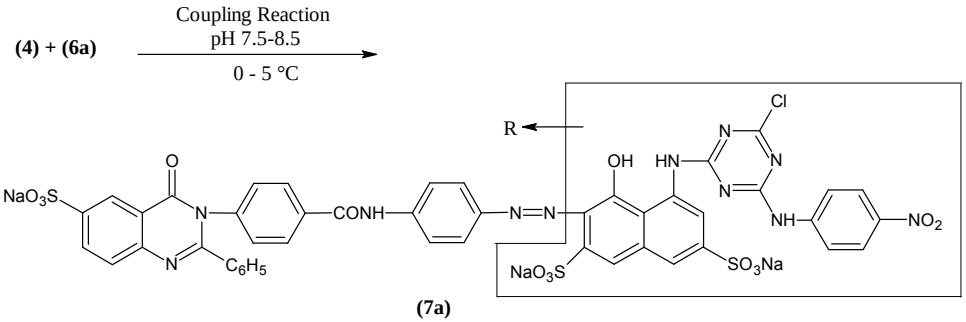
*Condensation with 4-nitro aniline (preparation of 4-nitro anilino cyanurated H-acid **6a**)*

The temperature of the ice-cooled well-stirred solution of cyanurated H-acid **5** (4.67 g, 0.01 mol) was gradually raised to 45 °C in about 30 min. To this cyanurated H-acid, 4-nitro aniline (1.38 g, 0.01 mol) was added dropwise at the same temperature, during a period of 30 min, maintaining the pH neutral by the simultaneous addition of sodium bicarbonate (1 % w/v). After completion of the addition, stirring was continued for a further 3 h. The thus obtained 4-nitro anilino cyanurated H-acid solution was subsequently used for the further coupling reaction. (The general route for the preparation of compound **6a** is outlined in Scheme 4).

*Formation of the dye **7a***

To an ice cold and stirred solution of 4-nitro anilino cyanurated H-acid **6a** (5.68 g, 0.01 mol), a freshly prepared diazo solution **4** (2.8 g, 0.005 mol) was added dropwise over a period of 10–15 min. The pH was maintained at 7.5 to 8.5 by the simultaneous addition of sodium carbonate solution (10 % w/v). During the coupling, a purple solution was formed. The stirring was continued for 3–4 h, maintaining the temperature below 5 °C. The reaction mixture was heated to 60 ºC and sodium chloride was added until a coloured material precipitated.

The mixture was stirred for 1 h, filtered and washed with a small amount of sodium chloride solution (5 % w/v). The solid was dried at 80–90 °C and extracted with DMF. The dye was precipitated by diluting the DMF-extract with excess chloroform. The violet dye was then filtered, washed with chloroform and dried at 60 °C. Yield: 85 %. (The general route for the preparation of compound (**7a**) is outlined in Scheme 5).



(7a)

Scheme 5. Synthetic route to dye **7a** (R: different 4-nitro aniline cyanurated coupling components (**6a**–**m**)).

Following the above-described procedure, other reactive dyes **7b**–**m** were synthesized using the required 4-nitro anilino cyanurated coupling components, *i.e.*, Gamma acid (**6b**), J-acid (**6c**), *N*-methyl-J-acid (**6d**), *N*-phenyl-J-acid (**6e**), Chicago acid (**6f**), Laurant acid (**6g**), Bronner acid (**6h**), Tobias acid (**6i**), sulpho Tobias acid (**6j**), Peri acid (**6k**), Koch acid (**6l**) and K-acid (**6m**).

CONCLUSIONS

Reactive dyes based on 2-phenyl- 3-{4'-[*N*-(4"-aminophenyl)carbamoyl]--phenyl}-quinazoline-4-(3*H*)-one-6-sulphonic acid were synthesized. These dyes give mostly pink, yellow and brown shades on silk, wool and cotton fabric having good to excellent washing fastness properties. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes for the fabrics. Exhaustion and fixation of these dyes are very good, which indicates that the dyes have good affinity and solubility with the fabrics. The presence of the quinazolinone structure in the dye molecules results in low sublimation and high thermal stability.

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ИЗВОД

НОВЕ АЗО БОЈЕ ДОБИЈЕНЕ ИЗ 2-ФЕНИЛ-3-{4'-[*N*-(4"-АМИНОФЕНИЛ)КАРБАМОИЛ]--ФЕНИЛ}-КИНАЗОЛИН-4-(3*H*)-ОН-6-СУЛФОНСКЕ КИСЕЛИНЕ

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Серија нових хетероцикличних моно азо реактивних боја **7a–m** добијена је куповањем производа диазотовања 2-фенил-3-{4'-[*N*-(4"-аминофенил)карбамоил]-фенил}-киназолин-4--(3*H*)-он-6-сулфонске киселине (**3**) са различитим цијануринским компонентама за куповање (**6a**–**m**) и испитиване су њихове способности бојења свиле, вуне и памука. Утврђено је да ове боје дају различиту покривеност са добром дубином и нијансом бојења влакана. Сва једињења окарактерисана су уобичајеним спектроскопским методама (IC и NMR) и елементалном анализом. Обојена влакна имају добру постојаност према светлу, прању и трљању.

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