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Synthesis and studies on chromene based reactive azo dyes and their applications on different fabrics

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ABSTRACT

A number of reactive azo dyes based on chromene moiety were prepared through two inversed routes using 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile, which when coupled to different diazonium salts, yielded the corresponding dyes which were then further reacted with cyanuric chloride. The structures of the prepared dyes were elucidated from their spectral data, elemental analyses and colour measurements. Dyeing of cellulosic and nylon fibers using the prepared dyes was done under suitable conditions. Some properties of the prepared dyes such as fastness properties (washing, rubbing and perspiration) and colour measurements were investigated. The dyes showed very good fastness to washing properties when attached to nylon fibers but poor fastness to light properties were shown.

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1. Introduction

A versatile number of heterocyclic compounds are widely used in dye chemistry especially azo dyes ones. Azo dyes containing heterocyclic moieties show brighter and often deeper shades than their benzene analogs. On the other hand, such type of dyes are quite important as disperse dyes which used for dyeing polyester fibers; also, they are important as functional dye, nonlinear optical systems, photodynamic therapy and lasers [1-7]. From the heterocycles used for synthesis of azo dyes are chromene derivatives commonly used for production of highly effective fluorescent dyes for synthetic fibers and daylight fluorescent pigments [8-13]. Among azo dyes, reactive ones have an important place and could be used for dyeing various fabrics.

Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds to fibers. These bonds formed between a carbon atom or phosphorus atom of the dyes ion or molecules and an oxygen atom, nitrogen atom or sulfur atom of a hydroxyl, an amino or a mercapto group, respectively, of the substrate [14]. These dyes are generally used on higher value clothes, which are normally mercerized [15].

Reactive dyes though late entry into the field of synthetic dyes, very soon attained a commercial status. Several new reactive systems have been introduced from time to time, which covers the subject of innumerable patents and publication [16]. It was for the first time that dyeing has been done by chemical reaction between the dye and the fiber, enabling one to get assortment of bright, attractive shades of adequate fastness with considerable ease of dyeing.

Moreover, reactive dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. Reactive dyes are one of the most commonly used dyes for textile printing because of their high wet fastness, brilliant colors and variety of hue [17]. In general, reactive dyes used in printing often have a degree of fixation of only 60%, whereas in dyeing, a degree of fixation of over 90% can be achieved [18]. A large number of reactive dyes are azo compounds that are linked by an azo bridge [19]. Reactive dyes are extensively used in many industries such as textiles, rubber, paper, leather cosmetics and pharmaceuticals. In addition, they are characterized by ease of applications and minimum energy consumption.

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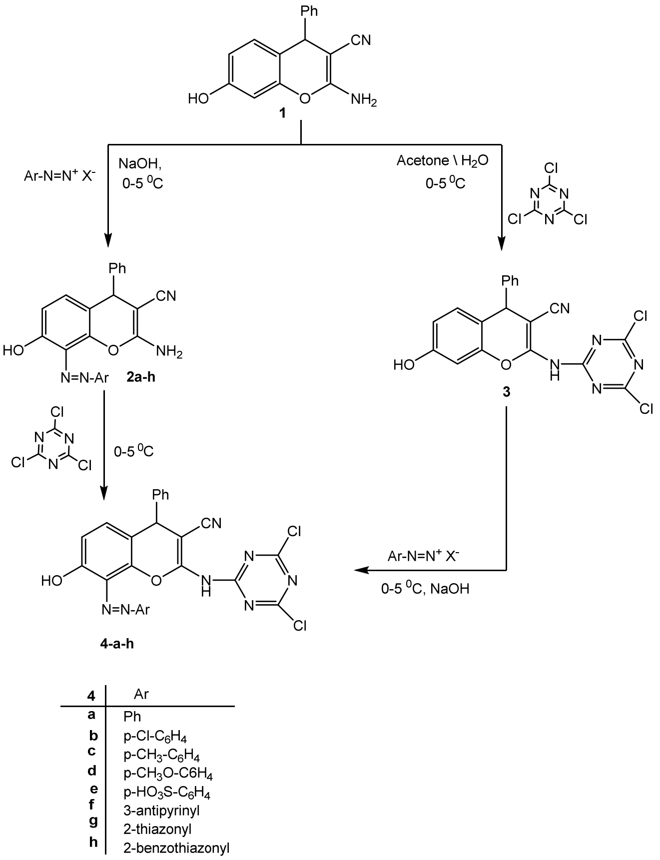

4	Ar
a	Ph
b	p-Cl-C6H4
c	p-CH3-C6H4
d	p-CH3O-C6H4
e	p-HO3S-C6H4
f	3-antipyrinyl
g	2-thiazonyl
h	2-benzothiazonyl

Scheme 1

For these reasons, herein, we reported a synthesis of number of new reactive azo dyes starting from 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**1**) through different alternative pathways.

2. Experimental

2.1. Instrumentation

Melting points were measured on Electrothermal IA 9000 series digital melting point apparatus. The IR spectra were recorded in potassium bromide discs on a Pye Unicam SP 3300 and Shimadzu FT-IR 8101 PC infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d_6) using a Varian Gemini 300 NMR spectrometer (300 MHz for ^{1}H NMR). Mass spectra were recorded on a Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. Elemental analysis was carried out at the Microanalytical Centre of Cairo University, Giza, Egypt. All reactions were followed by TLC (Silica gel, Merck).

2.2. Synthesis

2-Amino-4-phenyl-7-hydroxychromene-3-carbonitrile [20, 21] was prepared as reported in the literature.

2.2.1. Synthesis of 2-amino-8-arylazo-4-phenyl-7-hydroxy chromene-3-carbonitrile (2a-h)

To an ice cold solution of the appropriate aromatic amine (0.01 mol) in a mixture of concentrated hydrochloric acid (12 mL), and water (15 mL), a cold aqueous solution of sodium nitrite (0.7 g), was added portion wise at 0 °C. The solution was stirred vigorously for 1 h to yield the diazonium salt solution at 0-2 °C. The diazonium salt solution was then added drop wise to pre-cooled (0 °C) solution of compound **1** (2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile) (0.01 mol, 2.64 g in 10 mL ethanol and 5 mL of 10% NaOH) over a period of 1 h with vigorous stirring at 0-3 °C. The reaction mixture was further stirred for 1 h at 0-5 °C. After completion of the reaction, the products were filtered off, washed with water until free from acid, dried at 40 °C in an oven to give compounds **2a**-**h**, which were recrystallized from appropriate solvent (Scheme 1). The synthesized compounds **2a**-**h** together with their physical and spectral data are listed below.

2-Amino-7-hydroxy-4-phenyl-8-(phenyldiazenyl) -4H-chromene-3-carbonitrile (**2a**): Color: Orange. Yield: 72%. M.p.: 172-174 °C. FT-IR (KBr, ν, cm^{-1}): 1604 (C=N), 2189 (CN), 3237, 3347 (NH$_2$), 3440 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.92 (s, 1H, Chromene H-4), 6.24 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.89 (d, 1H, *J* = 9.1 Hz, H-6 Ar), 7.13-7.65 (m, 10H, ArH),7.74 (d, 1H, *J* = 9.1 Hz, H-5 Ar), 11.09 (s, 1H, D$_2$O exchangeable, OH). MS (EI, *m/z* (%)): 368 (M$^+$, 35), 318 (32), 197 (35), 118 (32), 93 (100). Anal. calcd. for $C_{22}H_{16}N_4O_2$: C, 71.73; H, 4.38; N, 15.21. Found C, 71.56; H, 4.28; N, 15.04%.

2-Amino-8-((4-chlorophenyl)diazenyl) -7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (**2b**): Color: Orange. Yield: 74%. M.p.: 188-190 °C. FT-IR (KBr, ν, cm^{-1}): 1621 (C=N), 2212(CN), 3198, 3325 (NH$_2$), 3392 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.84 (s, 1H, Chromene H-4), 6.37 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.84 (d, 1H, *J* = 9.1 Hz, H-6 Ar), 7.10-7.68 (m, 9H, ArH),7.89 (d, 1H, *J* = 9.1 Hz, H-5 Ar), 12.06 (s, 1H, D$_2$O exchangeable, OH). MS (EI, *m/z* (%)): 404 (M$^+$, 10), 402 (M$^+$, 27), 265 (48), 197 (100), 111 (53), 69 (70). Anal. calcd. for $C_{22}H_{15}ClN_4O_2$: C, 65.60; H, 3.75; N, 13.91. Found C, 65.50; H, 3.67; N, 13.64%.

2-Amino-7-hydroxy-4-phenyl-8-(p-tolyldiazenyl) -4H-chromene-3-carbonitrile (**2c**):Color: Orange. Yield: 75%. M.p.: 167-169 °C. FT-IR (KBr, ν, cm^{-1}): 1606 (C=N), 2188(CN), 3212, 3340 (NH$_2$), 3423 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.37 (s, 3H, CH$_3$), 4.87 (s, 1H, Chromene H-4), 6.48 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.84 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.11-7.67 (m, 9H, ArH),7.70 (d, 1H, J = 9.1 Hz, H-5 Ar), 12.01 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 382 (M$^+$, 76), 337 (100), 299 (89), 248 (75), 128 (86), 116 (73), 60 (89). Anal. calcd. for $C_{23}H_{18}N_4O_2$: C, 72.24; H, 4.74; N, 14.65. Found C, 72.12; H, 4.56; N, 14.47%.

2-Amino-7-hydroxy-8-((4-methoxyphenyl)diazenyl) -4-phenyl-4H-chromene-3-carbonitrile (**2d**): Color: Orange. Yield: 73%. M.p.: 147-149 °C. FT-IR (KBr, ν, cm^{-1}): 1623 (C=N), 2189(CN), 3216, 3335 (NH$_2$), 3425 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.77 (s, 3H, CH$_3$), 4.88 (s, 1H, Chromene H-4), 6.52 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.82 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.16-7.68 (m, 9H, ArH),7.73 (d, 1H, J = 9.1 Hz, H-5 Ar), 11.94 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 398 (M$^+$, 34), 336 (52), 243 (50), 187 (83), 147 (47), 77 (100). Anal. calcd. for $C_{23}H_{18}N_4O_3$: C, 69.34; H, 4.55; N, 14.06. Found C, 69.18; H, 4.50; N, 13.91%.

4-((2-Amino-3-cyano-7-hydroxy-4-phenyl-4H-chromen-8-yl) diazenyl)benzenesulfonic acid (**2e**): Color: Orange. Yield: 70%. M.p.: 212-214 °C. FT-IR (KBr, ν, cm^{-1}): 1621 (C=N), 2190(CN), 3247, 3329 (NH$_2$), 3426 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.89 (s, 1H, Chromene H-4), 6.27 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.88 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.17-7.68 (m, 9H, ArH),7.77 (d, 1H, J = 9.1 Hz, H-5 Ar), 9.34, 12.06 (s, 2H, D$_2$O exchangeable, OH and SO$_3$H). MS (EI, m/z (%)): 448 (M$^+$, 66), 391 (70), 272 (64), 191 (70), 151 (71), 134 (79), 64 (100). Anal. calcd. for $C_{22}H_{16}N_4O_5S$: C, 58.92; H, 3.60; N, 12.49. Found C, 58.78; H, 3.46; N, 12.32%.

2-Amino-8-((1, 5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl) -7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (**2f**): Color: Orange. Yield: 72%. M.p.: 181-183 °C. FT-IR (KBr, ν, cm^{-1}): 1621 (C=N), 1678 (C=O), 2189(CN), 3189, 3364 (NH$_2$), 3432 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.32 (s, 3H, CH$_3$), 3.23 (s, 3H, CH$_3$), 4.88 (s, 1H, Chromene H-4), 6.48 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.86 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.17-7.72 (m, 10H, ArH), 7.82 (d, 1H, J = 9.1 Hz, H-5 Ar), 12.01 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 478 (M$^+$, 58), 459 (79), 380 (56), 231 (78), 199 (72), 111 (70), 55 (100). Anal. calcd. for $C_{27}H_{22}N_6O_3$: C, 67.77; H, 4.63; N, 17.56. Found C, 67.90; H, 4.68; N, 17.38%.

2-Amino-7-hydroxy-4-phenyl-8-(thiazol-2-yldiazenyl) -4H-chromene-3-carbonitrile (**2g**): Color: Orange. Yield: 74%. M.p.: 193-195 °C. FT-IR (KBr, ν, cm^{-1}): 1621 (C=N), 2211(CN), 3217, 3336 (NH$_2$), 3422 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.83 (s, 1H, Chromene H-4), 6.47 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.87 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.25-7.88 (m, 7H, ArH), 7.97 (d, 1H, J = 9.1 Hz, H-5 Ar), 11.33 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 375 (M$^+$, 16), 321 (38), 244 (39), 177 (61), 95 (24), 69 (100). Anal. calcd. for $C_{19}H_{13}N_5O_2S$: C, 60.79; H, 3.49; N, 18.66. Found C, 60.49; H, 3.51; N, 18.42%.

2-Amino-8-(benzo[d]thiazol-2-yldiazenyl)-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (**2h**): Color: Orange. Yield: 76%. M.p.: 152-154 °C. FT-IR (KBr, ν, cm^{-1}): 1624 (C=N), 2190(CN), 3220, 3343 (NH$_2$), 3427 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.84 (s, 1H, Chromene H-4), 6.42 (s, 2H, D$_2$O exchangeable, NH$_2$), 6.82 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.21-7.87 (m, 9H, ArH), 7.92 (d, 1H, J = 9.1 Hz, H-5 Ar), 11.26 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 425 (M$^+$, 58), 386 (59), 313 (58), 272 (47), 191 (56), 125 (68), 55 (87). Anal. calcd. for $C_{23}H_{15}N_5O_2S$: C, 64.93; H, 3.55; N, 16.46. Found C, 64.76; H, 3.46; N, 16.43%.

2.2.2. Synthesis of 2-((4,6-dichloro-1,3,5-triazin-2-yl)amino) -7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (3)

A solution of cyanuric chloride (3.66 g, 0.02 mol) in acetone (30 mL) was poured into a vigorously stirred mixture of crushed ice (50 g) and water (50 mL). A solution of compound **1** (5.28 g, 0.02 mol) was added drop wise at 0-5 °C, over 60 min, with the pH maintained between 3.5 and 4.5 using sodium carbonate solution (10%, *w:v*). The solution was stirred for a further 60 min to complete the reaction. The product formed during the reaction was removed by filtration, washed with water several times, dried and crystallized from ethanol to give compound **3** (Scheme 1). Color: Creamy white. Yield: 81%. M.p.: 163-165 °C. FT-IR (KBr, ν, cm^{-1}): 1605 (C=N), 2189(CN), 3335 (NH), 3422 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.73 (s, 1H, Chromene H-4), 6.31(s, 1H, D$_2$O exchangeable, NH), 6.67(s, 1H, Ar-H(8)), 6.89 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.31-7.65 (m, 5H, Ar-H),7.76 (d, 1H, J = 9.1 Hz, H-5 Ar), 11.09 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 411 (M$^+$, 16), 357 (38), 280 (39), 213 (61), 131(24), 105 (100). Anal. calcd. for $C_{19}H_{11}Cl_2N_5O_2$: C, 55.36; H, 2.69; N, 16.99. Found C, 55.32; H, 2.56; N, 16.68%.

2.2.3. Synthesis of 2-(4,6-dichloro-[1,3,5]triazin-2-ylamino)-8-arylazo-7-hydroxy-4-phenylchromene-3-carbonitrile (4a-h)

Method A: A solution of cyanuric chloride (0.915 g, 0.005 mol) in acetone (20 mL) was poured into a vigorously stirred mixture of crushed ice (50 g) and water (30 mL). A solution of compound **2a-h** (0.005 mol) was added dropwise at 0-5 °C, over 60 min, with the pH maintained between 3.5 and 4.5 using sodium carbonate solution (10%, *w:v*). The solution was stirred for a further 60 min to complete the reaction. The product formed during the reaction was removed by filtration, washed with water several times, dried and crystallized from appropriate solvent to give compounds **4a-h** (Scheme 1).

Method B: To an ice cold solution of the appropriate aromatic amine (0.001 mol) in a mixture of concentrated hydrochloric acid (7 mL) and water (15 mL), a cold aqueous solution of sodium nitrite (0.1 g), was added portion wise at 0 °C. The solution was stirred vigorously for 1 hr to yield the diazonium salt solution at 0-2 °C. The diazonium salt solution was then added drop wise to pre-cooled (0 °C) solution of compound **3** (0.001 mol, 0.411 g in 10 mL ethanol and 3 mL of 10% NaOH) over a period of 1 hr with vigorous stirring at 0-3 °C. The reaction mixture was further stirred for 1 hr at 0-5 °C. After completion of the reaction, the products were filtered off, washed with water until free from acid, dried at 40 °C in an oven to give compound **4a-h** (Scheme 1). The synthesized compounds **4a-h** together with their physical and spectral data are listed below.

2-((4,6-Dichloro-1,3,5-triazin-2-yl)amino)-7-hydroxy-4-phenyl-8-(phenyldiazenyl)-4H-chromene-3-carbonitrile (**4a**): Color: Orange. Yield: 68%. M.p.: 220-222 °C. FT-IR (KBr, ν, cm^{-1}): 1602 (C=N), 2190 (CN), 32145 (NH), 3432 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.92 (s, 1H, Chromene H-4), 6.83 (d, 1H, J = 9.2 Hz, H-6 Ar), 7.09-7.60 (m, 10H, ArH), 7.78 (d, 1H, J = 9.2 Hz, H-5 Ar), 9.54 (s, 1H, D$_2$O exchangeable, NH), 11.21 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 518 (M$^+$+2, 50), 517 (M$^+$+1, 49), 516 (M$^+$, 95), 421 (84), 302 (82), 232 (69), 165 (75), 93 (100), 77 (67). Anal. calcd. for $C_{25}H_{15}Cl_2N_7O_2$: C, 58.15; H, 2.93; N, 18.99. Found C, 58.12; H, 2.76; N, 18.67%.

8-((4-Chlorophenyl)diazenyl)-2-((4,6-dichloro-1,3,5-triazin-2-yl) amino) -7-hydroxy-4-phenyl-4H-chromene -3-carbonitrile (**4b**): Color: Orange. Yield: 68%. M.p.: 172-173 °C. FT-IR (KBr, ν, cm^{-1}): 1601 (C=N), 2192 (CN), 3237 (NH), 3419 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.87 (s, 1H, Chromene H-4), 6.71 (d, 1H, J = 9.2 Hz, H-6 Ar), 7.10-7.64 (m, 9H, ArH), 7.78 (d, 1H, J = 9.2 Hz, H-5 Ar), 10.04 (s, 1H, D$_2$O exchangeable, NH), 11.32 (s, 1H, D$_2$O exchangeable, OH). MS (EI, m/z (%)): 552

(M^++2, 12), 551 (M^++1, 27), 550 (M^+, 33), 404 (58), 303 (48), 254 (40), 197 (69), 80 (92), 64 (100). Anal. calcd. for $C_{25}H_{14}Cl_3N_7O_2$: C, 54.52; H, 2.56; N, 17.80. Found C, 54.44; H, 2.38; N, 17.62%.

2-((4,6-Dichloro-1,3,5-triazin-2-yl)amino)-7-hydroxy-4-phenyl-8-(p-tolyldiazenyl)-4H-chromene-3-carbonitrile (**4c**): Color: Orange. Yield: 67%. M.p.: 193-195 °C. FT-IR (KBr, ν, cm^{-1}): 1584 (C=N), 2191 (CN), 3241 (NH), 3440 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.32 (s, 3H, CH_3), 4.97 (s, 1H, Chromene H-4), 6.86 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.11-7.68 (m, 9H, ArH), 7.73 (d, 1H, J = 9.1 Hz, H-5 Ar), 10.01 (s, 1H, D_2O exchangeable, NH), 11.12 (s, 1H, D_2O exchangeable, OH). MS (EI, *m/z* (%)): 530 (M^+, 46), 432 (46), 334 (38), 262 (50), 174 (33), 80 (94), 64 (100). Anal. calcd. for $C_{26}H_{17}Cl_2N_7O_2$: C, 58.88; H, 3.23; N, 18.49. Found C, 58.59; H, 3.20; N, 18.32%.

2-((4,6-Dichloro-1,3,5-triazin-2-yl)amino)-7-hydroxy-8- ((4-methoxyphenyl)diazenyl)-4-phenyl-4H-chromene-3-carbonitrile (**4d**): Color: Yellow. Yield: 72%. M.p.: 158-160 °C. FT-IR (KBr, ν, cm^{-1}): 1601 (C=N), 2190 (CN), 3278 (NH), 3442 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.87 (s, 3H, CH_3), 4.83 (s, 1H, Chromene H-4), 6.88 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.11-7.85 (m, 9H, ArH), 7.97 (d, 1H, J = 9.1 Hz, H-5 Ar), 10.23 (s, 1H, D_2O exchangeable, NH), 11.13 (s, 1H, D_2O exchangeable, OH). MS (EI, *m/z* (%)): 546 (M^+, 8), 488 (10), 336 (8), 282 (11), 158 (12), 80 (100), 64 (70). Anal. calcd. for $C_{26}H_{17}Cl_2N_7O_3$: C, 57.16; H, 3.14; N, 17.95. Found C, 57.03; H, 3.12; N, 17.76%.

4-((3-Cyano-2-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino) -7-hydroxy-4-phenyl-4H-chromen-8-yl) diazenyl) benzenesulfonic acid (**4e**): Color: Red. Yield: 66%. M.p.: 166-168 °C. FT-IR (KBr, ν, cm^{-1}): 1600 (C=N), 2192 (CN), 3241 (NH), 3424 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.90 (s, 1H, Chromene H-4), 6.86 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.18-7.74 (m, 9H, ArH), 7.84 (d, 1H, J = 9.1 Hz, H-5 Ar), 10.12 (s, 1H, D_2O exchangeable, NH), 11.14, 13.14 (s, 2H, D_2O exchangeable, OH and SO_3H). MS (EI, *m/z* (%)): 595 (M^+, 54), 467 (68), 384 (45), 238 (59), 153 (60), 80 (100), 64 (66). Anal. calcd. for $C_{25}H_{15}Cl_2N_7O_5S$: C, 50.35; H, 2.54; N, 16.44. Found C, 50.22; H, 2.34; N, 16.23%.

2-((4,6-Dichloro-1,3,5-triazin-2-yl)amino)-8-((1, 5-dimethyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazol-4-yl) diazenyl)-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (**4f**): Color: Yellow. Yield: 69%. M.p.: 201-203 °C. FT-IR (KBr, ν, cm^{-1}): 1611 (C=N), 1678 (C=O), 2189(CN), 3360 (NH), 3430 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.34 (s, 3H, CH_3), 3.28 (s, 3H, CH_3), 5.10 (s, 1H, Chromene H-4), 6.84 (d, 1H, J = 9.3 Hz, H-6 Ar), 7.11-7.79 (m, 10H, ArH), 7.88 (d, 1H, J = 9.3 Hz, H-5 Ar), 10.04 (s, 1H, D_2O exchangeable, NH), 11.87 (s, 1H, D_2O exchangeable, OH). MS (EI, *m/z* (%)): 626 (M^+, 14), 496 (27), 357 (16), 231 (18), 199 (22), 80 (100), 64 (66). Anal. calcd. for $C_{30}H_{21}Cl_2N_9O_3$: C, 57.52; H, 3.38; N, 20.12. Found C, 57.36; H, 3.24; N, 20.02%.

2-((4, 6-Dichloro-1, 3, 5-triazin-2-yl)amino)-7-hydroxy-4-phenyl-8-(thiazol-2-yldiazenyl) -4H-chromene-3-carbonitrile (**4g**): Color: Brown. Yield: 66%. M.p.: 184-186 °C. FT-IR (KBr, ν, cm^{-1}): 1613 (C=N), 2210(CN), 3326 (NH), 3409 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 5.23 (s, 1H, Chromene H-4), 6.87 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.15-7.82 (m, 7H, ArH), 7.92 (d, 1H, J = 9.1 Hz, H-5 Ar), 10.27 (s, 1H, D_2O exchangeable, NH), 11.26 (s, 1H, D_2O exchangeable, OH). MS (EI, *m/z* (%)): 523 (M^+, 17), 388 (68), 269 (79), 151 (68), 80 (93), 64 (100). Anal. calcd. for $C_{22}H_{12}Cl_2N_8O_2S$: C, 50.49; H, 2.31; N, 21.41. Found C, 50.37; H, 2.38; N, 21.29%.

8-(Benzo[d]thiazol-2-yldiazenyl)-2-((4, 6-dichloro-1, 3, 5-triazin-2-yl)amino) -7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (**4h**): Color: Yellow. Yield: 68%. M.p.: 210-212 °C. FT-IR (KBr, ν, cm^{-1}): 1614 (C=N), 2217(CN), 3358 (NH), 3426 (OH). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.73 (s, 1H, Chromene H-4), 6.84 (d, 1H, J = 9.1 Hz, H-6 Ar), 7.12-7.79 (m, 9H, ArH), 7.93 (d, 1H, J = 9.1 Hz, H-5 Ar), 10.16 (s, 1H, D_2O exchangeable, NH), 11.21 (s, 1H, D_2O exchangeable, OH). MS (EI, *m/z* (%)): 573 (M^+, 45), 501 (100), 459 (76), 358 (70), 260 (70), 190 (88), 82 (93), 60 (10). Anal. calcd. for $C_{26}H_{14}Cl_2N_8O_2S$: C, 54.46; H, 2.46; N, 19.54. Found C, 54.40; H, 2.23; N, 19.33%.

2.3. Dyeing

2.3.1. Materials

All chemicals were laboratory reagent grade. Bleached 100% cotton fabric (140 g/m^2) was supplied by El-Mahalla El-Kobra Company. The fabrics were scoured in aqueous solution with a liquor ratio1:50 containing 5 g/L nonionic detergent solution (Hostapal, Clariant) and 2 g/L Na_2CO_3 at 95 °C for 4 h to remove impurities, then rinsed thoroughly in cold tap water, and dried at room temperature. Bleached 100% nylon fabric (129 g/m^2) was supplied by El-Mahalla El-Kobra Company. The fabrics were scoured in aqueous solution with a liquor ratio1:50 containing 5 g/L nonionic detergent solution (Hostapal, Clariant) at 50 °C for 30 min to remove impurities, then rinsed thoroughly in cold tap water, and dried at room temperature.

2.3.2. Dyeing of cotton with dichlorotriazine reactive dyes

Dyeing process was carried out at 40 °C, Liquor to goods ratio (L.R.) 1:30 deing bath contains 2% weight of fiber (w.o.f) dye, sodium chloride 35 g/L, the fabric were immersed and the temperature were raised to 40 °C. The alkali sodium carbonate 30 g/L was added after 30 min and the dyeing continued for another 30 min. At the end of dyeing, the dyed samples were rinsed with tap water and allowed to dry in open air.

2.3.3. Dyeing of nylon with hydrolyzed reactive dye

Dyeing process was carried out at 95 °C. Dyeing bath pH adjusted to 5 using acetic acid solution. The dyeing continued for 60 min. At the end of dyeing, the dyed samples were rinsed with tap water and allowed to dry in open air.

3. Results and discussion

3.1. Chemistry

In general, azo dyes have been prepared through various pathways either by diazotization or other alternative methods [22,23]. In the present work, a series of chromene based reactive azo dyes were prepared using the compound **1** as a coupling component with different diazotized aromatic and heteroaromatic amines. The phenolic ring of compound **1** is quite much reactive towards electrophilic reagents such as diazonium salts and two possible positions can couple with the attacking electrophilic diazonium salt. These positions are 6 and 8, however, indeed one position only coupled to the reagent (position 8) [24]. Aromatic and heteroaromatic amines were converted into diazonium salts then coupled to the chromene compound **1** in faintly basic medium (NaOH) to produce the azo dyes **2a**-**h**. The resulting dyes themselves are not the main target of this project but they could be used in further treatment for production of newly reactive dyes. The use of 2,4,6-trichlorotriazine (cyanauric chloride) can fulfill the required purpose which can act as an intervening unit between the dye molecule and polymeric fibrous material such as cotton and wool.

For the preparation of the required reactive dyes, two synthetic routes could be followed which could be considered as reverse of each other. First, aromatic and heteroaromatic amines were diazotized and then added portion wise to an alkaline solution of the chromene **1** to afford the dyes **2a**-**h**.

Table 1. Fastness properties of the dyed cotton fabrics with the reactive dyes [a].

Sample	Washing			Perspiration						Rubbing		Light
				Alkaline			Acidic					
	St.**	St.*	Alt.	St.**	St.*	Alt.	St.**	St.*	Alt.	Wet	Dry	
1	4	4	3-4	3-4	4	3-4	4	4	3-4	3	4	4
2	4	4	4	4	4	3-4	4	4	4	3-4	4	4
3	3-4	2-3	3-4	3-4	4	3	3-4	4	3	4	4	2
4	4	3-4	4	3-4	4	3-4	3-4	4	3-4	4	4	2
5	4	4	3	3-4	4	3-4	3-4	4	3-4	3-4	4	2
6	4	4	3	3-4	4	3	4	4	4	4	4	4
7	4	4	3	3-4	4	3	4	4	4	4	4	3-4

[a] Alt.: Alteration; St: Staining, * Staining on cotton; ** Staining on wool.

These dyes in turn reacted with 2,4,6-trichlorotriazine in a mixture of acetone and water at low temperature at pH = 7 and the products formed during the reaction separated by filtration to give the reactive azodyes **4a-h**.

The second route achieved by treating compound **1** with cyanauric chloride under same conditions as in the first route giving compound **3** which was coupled smoothly with various diazonium salts furnishing compounds **4a-h**. The second route thought to be better than the first one as it includes less reaction steps and thus saving chemicals.

3.2. Fastness properties [25-30]

3.2.1. Color fastness to washing

The color fastness to washing was determined according to the method ISO 105-C02 (1989) [31]. The composite specimens were sewed between two pieces of bleached cotton and wool fabrics, and then immersed into an aqueous solution containing 5 g/L non-ionic detergents at liquor ratio 1:50. The bath was thermostatically adjusted to 60 °C and 50 °C for cotton and nylon fabric, respectively, for 30 min. After the desired time, samples were removed, rinsed twice with occasional hand squeezing, and then dried. Evaluation of the wash fastness was established using the Grey-scale for color change 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

3.2.2. Color fastness to rubbing

Color fastness to rubbing was determined according to the test method ISO 105-X12 (1987) [32]. The test is designed for determining the degree of color, which may transfer from the surface of the colored fibers to other surface, by rubbing. The current test can be carried out on dry and wet fibers.

3.2.2.1. Dry crocking test

The test specimen was placed flat on the base of the crock-meter. A white testing cloth was mounted. The covered finger was lowered on to the test specimen and caused to slide back and forth 20 times by making ten complete turns at a rate of one turn/sec. The white test sample was then removed for evaluation using the Grey-scale for staining: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

3.2.2.2. Wet crocking test

The white test sample was thoroughly wetted out in water to a 65% and then picked up. The procedure was run as before. The white test samples were air dried before evaluation: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

3.2.3. Color fastness to perspiration

Two artificial perspiration solutions were prepared as follows according to test method ISO 105-E04 (1989) [33]; acidic and alkaline solutions.

Acidic solution was prepared by dissolving of L-histidine monohydrochloride monohydrate (0.5 g), sodium chloride (5 g) and sodium dihydrogen orthophosphate dihydrate (2.2 g) in one liter distilled water. Then the pH was finally adjusted to 5.5 using 0.1 N NaOH. To prepare the alkaline solution, L-histidine monohydrochloride monohydrate (0.5 g), sodium chloride (5 g) and disodium hydrogen orthophosphate dihydrate (2.5 g) were all dissolved in one liter distilled water. The pH was adjusted to 8 using 0.1 N NaOH.

The fastness test was performed as follows. The colored specimen 5×4 cm was sewed between two pieces of uncolored specimens to form composite specimen. The composite samples were immersed for 15-30 min. in both solutions with a proper agitation and squeezing to insure complete wetting. The test specimens were placed between two plates of glass or plastic under a force of about 4-5 kg. The plates containing the composite specimens were then held vertical in an oven at 37±2 °C for 4 hours.

The effect on the color of the tested specimens was expressed and defined by reference to Grey-scale for color change: 1, poor; 2, fair; 3, moderate; 4, good; 5, excellent.

3.2.4. Color fastness to light

The light fastness test was carried out in accordance with test method ISO 105-B02 (1988) [34] using carbon arc lamp, continuous light, for 35 hours. The effect on the color of the tested samples was recorded by reference to Blue-scale for color change 1, poor; 3, moderate; 5, good; 8, very good [25].

3.2.5. Fastness properties

3.2.5.1. Fastness to washing

As shown in Table 1, the dyed cotton fabrics have very good fastness to washing according to international Geometric Grey scale with exception of dye **3** which gives fear result. Also, in Table 2, the dyed nylon fabrics have very good fastness to washing according to international Geometric Grey scale with exception of dye **3** which gives fear result as a result of surface coloration.

3.2.5.2. Fastness to perspiration (Acid and alkaline)

The high rating for change in the color at both acidic and alkaline conditions indicates that the sensitivity of the dyed samples is not related to pH. This may be due to the stability of the dyes towards degradation under either acidic or basic conditions.

3.2.5.3. Fastness to Rubbing

The test is designed to determine the amount of color transferred from the surface of colored fabrics to another surface by rubbing. Most of the dyes have a moderate rubbing fatness and this may be attributed to adequate diffusion of dye molecule into the fabrics.

Table 2. Fastness properties of the dyed nylon fabrics [a].

Sample	Washing			Perspiration						Rubbing		Light
				Alkaline			Acidic					
	St.**	St.*	Alt.	St.**	St.*	Alt.	St.**	St.*	Alt.	Wet	Dry	
1	4	3	4	3-4	4	4	4	4	4	3	3	3
2	4	4	4	3-4	4	4	4	4	4	3-4	4	3-4
3	3-4	2-3	3	3-4	4	3-4	4	4	4	2-3	2-3	2-3
4	4	3-4	4	3-4	4	3-4	4	4	3-4	2-3	3-4	2-3
5	4	4	3-4	3-4	4	3-4	4	4	4	2-3	3	2-3
6	4	4	4	4	4	4	4	4	4	3-4	4	3
7	4	4	4	3-4	4	4	4	4	4	3-4	3-4	3-4

[a] Alt.: Alteration; St: Staining; * Staining on cotton; ** Staining on wool.

3.2.5.4. Fastness to light

It is significantly depending on nature of the substituents which change the electron density around hydrazo group. Generally the light fastness is poor, this may be due to surface coloration.

4. Conclusion

A series of reactive azo-dyes were prepared through simple synthetic pathways and they applied to cotton and naylon fabrics and showed bad properties towards cotton fibers but good dying properties towards naylon fibers were observed.

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