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3-Arylazo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-ones as Azodisperse Dyes for Dyeing Polyester Fabrics

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Summary. Diazotized 3-amino-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one was coupled with various hydroxy aromatics to give the corresponding 3-arylazo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-ones in reasonable yields. The dyes produced were applied to polyesters as disperse dyes and their fastness properties were elevated.

Keywords. 3-Amino-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one; Diazonium salt; Disperse dyes; Fastness properties; Polyester.

Introduction

The unique biological activities and characteristic chemical structures have made synthesis studies of the quinazoline ring system attractive over the years. Synthesis of quinazoline derivatives provides the backbone for the synthesis of numerous compounds with pharmacological activities [1–9].

As part of our continuing interest in heterocyclic chemistry, we have reported simple and convenient approaches for the synthesis of various quinazolines [10–21]. We now report on the successful synthesis of some new 3-arylazo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-ones and their application as disperse dyes for dyeing polyester fabrics.

Results and Discussion

3-Amino-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one (**1**) was prepared according to Ref. [22]. Diazotization of **1** was performed by using a mixture of sodium nitrite and hydrochloric acid to produce the corresponding diazonium salt **2**. Coupling of **2** with several phenols, such as α-naphthol, β-naphthol, phenol, resorcinol, and 8-hydroxyquinoline in aqueous sodium hydroxide solution (10%) afforded the corresponding 3-arylazo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-ones **3**–**7** in moderate yields (50–54%; Scheme 1).

The structures of diazo dyes **3**–**7** were confirmed by various spectroscopic techniques including IR, ^{1}H NMR, mass, and accurate mass data. The IR spectra of **3**–**7** are characterized by the presence of absorption bands within the $\bar{\nu} = 3167$–$3300\,\text{cm}^{-1}$ region corresponding to the stretching vibrations of the NH group. The bands within the $\bar{\nu} = 1661$–$1666\,\text{cm}^{-1}$ region are due to the stretching vibration of the C=O group of the quinazolinone moiety. The absorption bands at the $\bar{\nu} = 1389$–$1410\,\text{cm}^{-1}$ region are due to the symmetric stretching vibrations of the azo group. Thus absorption bands within the $\bar{\nu} = 3386$–$3544\,\text{cm}^{-1}$ region are attributed to the phenolic OH group of the coupler moieties. The ^{1}H NMR spectra showed a characteristic NH signal in the $\delta = 13.11$–13.22 ppm region. The structures of diazo dyes **3**–**7** were confirmed further by mass and accurate mass data. The electron impact mass spectra indicated the presence of molecular ion peaks in all cases.

Dyeing of Polyester Fabrics and Dyeing Properties

Most influences that can affect fastness are light, washing, heat, perspiration, and atmospheric pollution.

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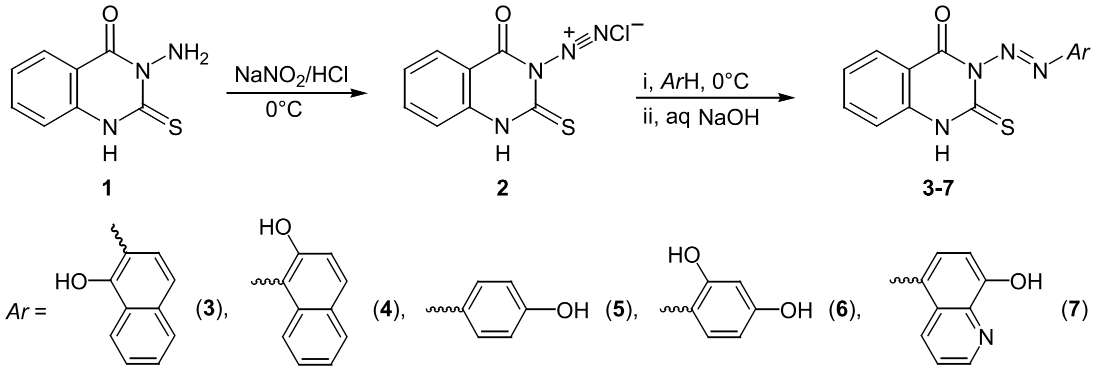

Scheme 1

Table 1. Fastness properties of dyes **3–7**

Compd.	Washing	Perspiration		Rubbing		Sublimation		Light (40 h)
		Acid	Alkali	Dry	Wet	Alt	St	
3	5–6	4	4–5	4	5	4	4	6
4	5–6	4–5	5	5	4	5	4	6
5	5	5	4	5	4	5	5	5
6	5–6	4–5	5	4	4	4	5	6
7	4–5	4	4	4	5	4	4	5

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

Conditions of such tests are chosen to correspond closely to the treatments employed in manufacture and of ordinary use conditions [23]. Results are given after usual matching of the tested samples against standard reference (the *Grey* scale) [23]. The results obtained are shown in Table 1. The results revealed that these dyes have good fastness properties.

In conclusion, a set of five useful disperse dyes **3**–**7** was synthesised by azo coupling. The dyes were investigated for their dyeing characteristics on polyester and showed good washing, perspiration, rubbing, sublimation, and light fastness. The remarkable degree of brightness after washings is indicative of good penetration and the excellent affinity of these dyes for the fabric due to the accumulation of polar groups.

Experimental

Melting points were determined on an electrothermal melting MEL-TEMP II apparatus. ^{1}H NMR spectra were recorded on CF_3COOD solutions using a Bruker AC400 spectrometer operating at 400 MHz. Low resolution mass spectra were recorded on a Quattro II triple quadrupole mass spectrometer (electron impact: 70 eV). Accurate mass data were obtained on a MAT 900 instrument. IR spectra were recorded on a Perkin-Elmer 1430 spectrometer. Compound **1** was prepared according to Ref. [22]. Its analytical data agreed with the published work.

Synthesis of 3-Arylazo-2-thioxo-2,3-dihydro-1H-quinazolin-4-ones **3**–**7**

A cold (0°C) solution of 0.7 g sodium nitrate in 10 cm^3 H_2O was added gradually to a cold (0°C) suspension of 1.93 g **1** (0.01 mol) in 5 cm^3 conc. HCl. The diazonium salt thus obtained was added with continuous stirring to a cold (0°C) solution of hydroxyaryl compounds (0.01 mole) in 20 cm^3 10% NaOH solution. The mixture was stirred at 0°C for 1 h, filtered, washed with H_2O, dried, and crystallized from glacial acetic acid to give the corresponding 3-arylazo-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-ones **3**–**7**.

3-(4-Hydroxynaphthylazo)-2-thioxo-2,3-dihydro-1H-quinazolin-4-one (**3**, $C_{18}H_{12}N_4O_2S$)

Yield 54%; yellow; mp 140–142°C; IR (KBr): $\bar{\nu} = 3386$ (OH), 3224 (NH), 1661 (C=O), 1400 (N=N), 1251 (C=S) cm^{-1}; ^{1}H NMR: $\delta = 6.72$–7.58 (m, 10H), 7.81 (dd, $J = 8.1$, 2.0 Hz, 1H), 13.20 (s, exch, 1H) ppm; EI-MS: m/z (%) = 348 (M^+, 7), 316 (3), 272 (3), 143 (14), 128 (16), 115 (34) 105 (100), 90 (16), 76 (20), 63 (30); HREI-MS: $C_{18}H_{12}N_4O_2S$ (M^+), calcd 348.0681, found 348.0682.

3-(2-Hydroxynaphthylazo)-2-thioxo-2,3-dihydro-1H-quinazolin-4-one (**4**, $C_{18}H_{12}N_4O_2S$)

Yield 51%; light pink; mp 230–231°C; IR (KBr): $\bar{\nu} = 3424$ (OH), 3300 (NH), 1662 (C=O), 1389 (N=N), 1252 (C=S) cm^{-1}; ^{1}H NMR: $\delta = 6.01$ (s, exch, 1H), 6.68–7.78 (m, 9H), 8.08 (d, $J = 7.8$ Hz, 1H), 13.14 (s, exch, 1H) ppm; EI-MS: m/z (%) = 348 (M^+, 21), 316 (12), 272 (5), 143 (11), 128 (31), 115 (47) 105 (100), 90 (22), 76 (17), 63 (26); HREI-MS: $C_{18}H_{12}N_4O_2S$ (M^+), calcd 348.0681, found 348.0684.

3-(4-Hydroxyphenylazo)-2-thioxo-2,3-dihydro-1H-quinazolin-4-one (**5**, $C_{14}H_{10}N_4O_2S$)

Yield 50%; light brown; mp 169–171°C; IR (KBr): $\bar{\nu} = 3544$ (OH), 3189 (NH), 1666 (C=O), 1410 (N=N), 1235 (C=S) cm^{-1}; ^{1}H NMR: $\delta = 5.67$ (s, exch, 1H), 6.64–7.31 (m, 7H), 7.78 (dd, $J = 8.2$, 2.1 Hz, 1H), 13.22 (s, exch, 1H) ppm; EI-MS: m/z (%) = 298 (M^+, 7), 266 (10), 251 (5), 242 (75), 197 (53), 137 (100) 93 (67), 76 (18); HREI-MS: $C_{14}H_{10}N_4O_2S$ (M^+), calcd 298.0524, found 298.0525.

3-(2,4-Dihydroxyphenylazo)-2-thioxo-2,3-dihydro-1H-quinazolin-4-one (**6**, $C_{14}H_{10}N_4O_3S$)

Yield 53%; brown; mp 299–302°C; IR (KBr): $\bar{\nu} = 3430$ (OH), 3167 (NH), 1661 (C=O), 1397 (N=N), 1224 (C=S) cm^{-1}; ^{1}H NMR: $\delta = 6.11$ (s, exch, 1H), 6.18–7.28 (m, 8H), 7.79 (d, $J = 8.2$ Hz, 1H), 13.18 (s, exch, 1H) ppm; EI-MS: m/z (%) = 314 (M^+, 12), 177 (8), 146 (65), 137 (100) 119 (22), 110 (2), 93 (12), 91 (18), 77 (10); HREI-MS: $C_{14}H_{10}N_4O_3S$ (M^+), calcd 314.3204, found 314.3205.

3-(8-Hydroxyquinolin-5-ylazo)-2-thioxo-2,3-dihydro-1H-quinazolin-4-one (**7**, $C_{17}H_{11}N_5O_2S$)

Yield 52%; dark yellow; mp 200–202°C; IR (KBr): $\bar{\nu} = 3395$ (OH), 3167 (NH), 1663 (C=O), 1403 (N=N), 1248 (C=S) cm^{-1}; ^{1}H NMR: $\delta = 6.61$–7.32 (m, 7H), 7.82 (dd, $J = 8.1$, 2.2 Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 1H), 9.01 (d, $J = 7.9$ Hz, 1H), 13.11 (s, exch, 1H) ppm; EI-MS: m/z (%) = 349 (M^+, 15), 274 (19), 176 (25), 144 (10), 116 (15), 105 (100) 90 (7), 77 (27), 63 (28); HREI-MS: $C_{17}H_{11}N_5O_2S$ (M^+), calcd 349.3677, found 349.3677.

Dyeing Procedure

The fabric was dyed with dye (2%, calculated by weight of the fabric) and Avolan IS (1%, Bayer AG, Germany) as dispersing agent, kept at a liquor ratio of 20:1. The process was started at 60°C, and the temperature was then raised to 130°C over 30 min and maintained there for 1 h. After cooling, the fabric was removed and then treated with a solution of $NaHSO_4$ (2%), NaOH (2%), and the dispersing agent Avolan IS (0.1%) at 70°C for 30 min. Finally, the fabric was rinsed and dried at 60°C.

Colour Fastness Tests

The results are collected in Table 1.

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

(ii) *Fastness to Perspiration.* The samples were prepared by stitching a piece of dyed polyester fabric between two pieces of undyed cotton fabric, all of equal length, and then immersed in the acid or alkaline solution for 30 min. The acid solution ($pH = 3.5$) contained sodium chloride ($10\,g \cdot dm^{-3}$), lactic acid ($1\,g \cdot dm^{-3}$), disodium orthophosphate ($1\,g \cdot dm^{-3}$), and histidine monohydrochloride ($0.25\,g \cdot dm^{-3}$). The alkaline solution ($pH = 8$) contained sodium chloride ($10\,g \cdot dm^{-3}$), NH_4Cl ($4\,g \cdot dm^{-3}$), disodium orthophosphate ($1\,g \cdot dm^{-3}$), and histidine monohydrochloride ($0.25\,g \cdot dm^{-3}$).

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

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

(v) *Fastness to Light.* Light fastness was determined by exposing the dyed polyester on a Xenotest 150 (Original Hanau, chamber temperature 25–30°C, black panel temperature 60°C, relative humidity 50–60%, dark glass (UV filter system) for 40 h.

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