Available online at www.sciencedirect.com
SCIENCE DIRECT®
Dyes and Pigments 60 (2004) 249–264
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis of new 5-thiazolyl azo-disperse dyes for dyeing polyester fabrics

M.A. Metwally[a], E. Abdel-latif[a], F.A. Amer[a], G. Kaupp[b,*]

[a]*University of Mansoura, Faculty of Science, Chemistry Department, Egypt*
[b]*University of Oldenburg, FB 9, Organische Chemie I, Germany*

Received 3 May 2003; accepted 25 June 2003

Abstract

Diazotized aryl amines were coupled with 2-aminothiazoles **1** and **2** to give the corresponding thiazolylazo dyes **3** and **4,** respectively. 2-Amino-5-arylazothiazoles **5** reacted with chloroacetyl chloride to afford the chloro-acetamide derivatives **6** which further reacted with 2-mercaptobenzothiazole to furnish a new series of 5-arylazothiazolyl dyes **7**. The azo structure of the dyes (rather than the tautomeric hydrazo structure) was assessed by ab initio DFT calculations at the B3LYP/6-31G* level. These dyes were applied to polyester fabric as disperse dyes and their fastness properties were evaluated.

Keywords: Aminothiazole; Antipyrine; Azo coupling; Chloroacetyl chloride; Disperse dyes; Polyester fabric; Fastness properties; DFT calculations

1. Introduction

2-Aminothiazole derivatives have long been used as precursors for the synthesis of biologically active molecules [1–4]. A large number of 2-aminothiazoles substituted with different aryl and hetraryl groups have been prepared for pharmaceutical purposes (for example antispasmodic [5] or antihistaminic [6] activity). In continuation of our previous work [7–11] on the synthesis of disperse dyes for dyeing polyester fabrics, the present paper describes the synthesis of several new 5-arylazothiazole derivatives and their applications as disperse dyes for dyeing polyester fabrics. It was of high interest to compare several thiazolyl azo-dyes substituted in the 4-position with phenyl and pyrazolonyl groups. We chose the 4-antipyrinyl moiety for that purpose.

2. Results and discussion

2.1. Synthesis of 5-arylazothiazole dyes

2-Aminothiazoles **1** and **2** [12–14], when coupled with a variety of aromatic diazonium salts in pyr-

* Corresponding author. Tel.: +49-441-798-3842; fax: +49-441-798-3409.
E-mail address: kaupp@kaupp.chemie.uni-oldenburg.de (G. Kaupp).

0143-7208/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0143-7208(03)00153-0

idine, yielded the corresponding 5-arylazothiazol-2-yl-phenylamines **3** and 5-arylazo-thiazolyl-2-yl-diphenylamines **4,** respectively. UV, IR, NMR and mass spectra have characterized the structure of these compounds. The IR spectra of **3A** exhibit bands at 3130–3173 (NH), 1601–1591 (C=C) and 1566–1555 cm^{-1}. The ^1H NMR spectrum of **3B-a** exhibits two singlet signals at $\delta = 2.40$ and 3.25 corresponding to the two methyl protons of the antipyrinyl-substituent, a multiplet at $\delta = 7.05$–7.70 due to the aromatic protons and a singlet at $\delta = 10.75$ due to the NH proton. The azo-structure of the dyes **3** (λ_{max} in the range of 458–512 nm) is secured by density functional theory (DFT) calculations at the B3LYP/6-31G* level that have the hydrazo tautomer of **3A-a** higher in energy by 3.7 kcal mol^{-1}. The dipole moment of the azo tautomer (1.38 Db) is predicted lower than the one calculated for the hydrazo structure (3.42 Db). However, this does not revert the stability in aqueous solutions as the calculated solvation energy in water decreases the energetic advantage by only 1.0 kcal mol^{-1}. In view of the minor influence of the substituent in the 4-position of the thiazole ring and the results listed in Tables 1 and 2, it can be judged that none of the dyes **3** accepts the hydrazone structure to a measurable extend. This conclusion is also secured by the comparison with **4**. These compounds have similar color properties (λ_{max} in the range of 460–521 nm) when compared to **3** (Fig. 1, and Tables 3 and 4).

2.2. Reaction of 2-amino-5-arylazothiazoles *5* with chloroacetyl chloride

2-Amino-5-arylazothiazoles **5** [15,16] were reacted with chloroacetyl chloride in DMF containing some drops of triethylamine to give the corresponding 2-(*N*-chloroacetyl)-5-(arylazo)thiazole derivatives **6**. The structure of the synthesized compounds was confirmed by the UV, IR, NMR and MS spectra. Tables 5 and 6 list the characteristics of the synthesized compounds. The infrared spectra revealed an intense band at 1707–1688 cm^{-1} assignable to the (C=O) stretching. The ^1H NMR spectrum of **6B-a** showed two singlets at $\delta = 2.40$ and 3.30 for two CH_3 groups, a singlet at $\delta = 4.30$ for the CH_2 group, a multiplet at $\delta = 7.35$–7.55 for

Table 1
Characterization data of the compounds **3A**

Dye	M.p./°C (solvent)	Yield/% (color)	UV, λ_{max} (MeOH)/nm ε/l mol^{-1} cm^{-1}	IR (KBr)/cm^{-1}	Mol. formula Mol. wt.
3A-a	186–187 (EtOH)	67 (red)	464 24,400	3173, 3058, 2911, 2849, 1591, 1555, 1519, 1477, 1455, 1408, 1327, 1294.	$C_{21}H_{16}N_4S$ 356
3A-b	204–205 (EtOH)	74 (red)	466 29,400	3133, 3026, 2905, 2845, 1598, 1562, 1526, 1485, 1418, 1328, 1305, 1291.	$C_{22}H_{18}N_4S$ 370
3A-c	210–211 (EtOH)	78 (red)	473 29,000	3130, 3029, 2907, 2833, 1592, 1566, 1525, 1484,1454, 1427, 1327, 1246.	$C_{22}H_{18}N_4OS$ 386
3A-d	254–255 (DMF)	84 (violet)	512 18,400	3280, 3064, 1601, 1543, 1509, 1469, 1399, 1320, 1291, 1241, 1185, 1145.	$C_{21}H_{15}N_5O_2S$ 401
3A-e	218–219 (EtOH)	81 (red)	476 29,100	3137, 3026, 2912, 2835, 1598, 1560, 1526, 1467,1407, 1374, 1327, 1302.	$C_{21}H_{15}BrN_4S$ 435

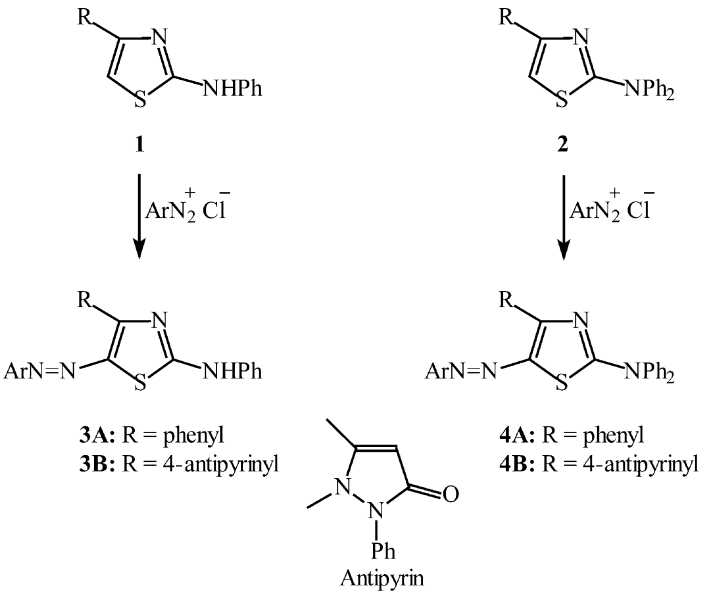

Fig. 1. Synthesis of the dyes **3** and **4**.

eight aromatic protons, a pseudo-doublet at $\delta = 7.75$ for two aromatic protons and a singlet (D_2O exchangeable) at $\delta = 12.70$ for the NH group.

2.3. Reaction of 5-arylazothiazoles *6* with 2-mercaptobenzothiazole

The chloroacetyl derivatives **6** were reacted with 2-mercaptobenzothiazole in the presence of ethanol containing a few drops of triethylamine to afford a series of compounds **7** in an effort to improve the dye fastness properties. The structure of the products was established via inspection of their spectral data (Tables 7 and 8). The IR spectra of the derivatives **7A** clearly indicate the presence of a carbonyl absorption band at $\nu = 1695$–$1683\ cm^{-1}$ and an N–H absorption band at 3172–$3148\ cm^{-1}$. Typically, the ^1H NMR spectrum of **7A-a** reveals the presence of a singlet peak at $\delta = 4.70$ due to the methylene protons in addition to a multiplet peak at $\delta = 7.50$–8.00 due to the aromatic protons (Fig. 2).

The compounds **6** and **7** assume the azo structure formulated. Their hydrazo tautomer structures (not formulated) have been judged to be more energetic by > 8.9 kcal mol^{-1} on the basis of DFT calculations at the B3LYP/6-31G* level with the N-acetyl model compound (**6A-a** with the Cl replaced by H) and it is not expected that very large differences in solvation energies will revert the situation. The hypsochromic effect (λ_{max} in the range of 410–468 nm) with respect to **3** and **4** is explained by the lower electron donating ability of the amide moiety.

2.4. Electronic absorption spectra

The electronic spectra of the 5-arylazothiazoles **3, 4, 6** and **7** were recorded in methanol and are listed in Tables 1–8. There is an intense band [ε: 20 000–30 000/l $mol^{-1}\ cm^{-1}$)] at λ_{max} values ranging from 410 to 512 nm in all cases. It was observed that the bathochromic shift by the substituents in the former diazonium component was in the following order $H \rightarrow CH_3 \rightarrow OCH_3 \approx Br \rightarrow NO_2$, with the shift of the NO_2-group being

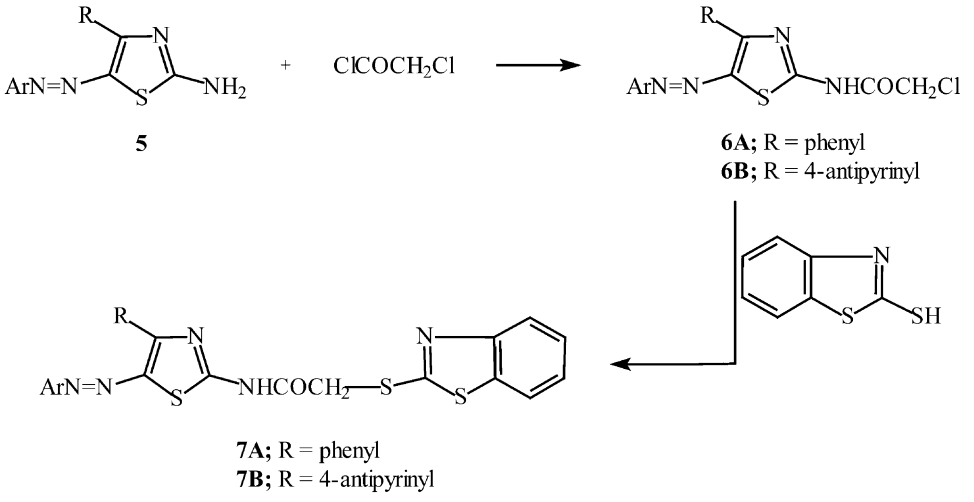

Fig. 2. Synthesis of the dyes **6** and **7**.

particularly large due to increased delocalization by the π-electron attraction of this substituent.

2.5. Dyeing of polyester fabric and dyeing properties

For some time an effort has been made to replace certain anthraquinone disperse dyes by new dyes often derived from hetraryl compounds. Useful dyes in this respect are derived from 2-aminothiazoles and 2-pyridones as coupling components or from 2-aminothiazoles, 2-amino-1,3,4-thiadiazoles, 5-amino-isothiazoles and 2-aminothiophenes as diazonium components.

The 5-arylazothiazoles **3, 4, 6** and **7** were synthesized to assess their dyeing properties and performance. The dyes were used for dyeing polyester fabric at 2% shade by high-temperature technique and gave generally deep and bright intense hues, ranging from yellow to red-violet.

2.5.1. Assessment of color fastness

Satisfactory color yields, compared with commercial dyes applied under similar conditions, were obtained at 2% depth, and excellent leveling and exhaustion of dye liquors were also achieved. Furthermore, the dyes gave excellent uniformity of coloration of polyester without the use of retarding agent. The results are listed in the Tables 10 and 11. The following generalizations can be drawn:

1. Excellent behavior is shown in the fastnesses to washings at 50 °C and to perspiration.
2. Most of the dyes have a good rubbing fastness (4); only a few of these dyes have moderate to poor rubbing fastness (dry and wet) and this may be attributed to inadequate diffusion of the dye molecules into the fabric.
3. Most of the dyes exhibit good sublimation fastness.
4. The light fastness of the 5-arylazo thiazole dyes **3, 4, 6** and **7** on polyester is significantly affected by the nature of the substituents in the diazonium component. The inclusion of electron-withdrawing (nitro or bromine) substituents improves the light fastness. In most cases, the best light fastness was obtained by the dyes containing a nitro group in the diazonium

Table 2
Characterization data of the compounds **3B**

Dye	M.p./°C (solvent)	Yield/% (color)	UV, λ_{max} (MeOH)/nm ε/l mol^{-1} cm^{-1}	IR (KBr)/cm^{-1}	Mol. formula Mol. wt.
3B-a	242 (MeOH)	80 (red)	458 25,400	3245, 3197, 3033, 1651, 1592, 1562, 1499, 1446, 1412, 1325, 1216, 3103.	$C_{26}H_{22}N_6OS$ 466
3B-b	239 (MeOH)	78 (red)	460 29,200	3269, 3197, 3050, 1647, 1581, 1560, 1499, 1446, 1414, 1336, 1258, 1201.	$C_{27}H_{24}N_6OS$ 480
3B-c	246 (MeOH)	81 (red)	466 29,500	3253, 3015, 1630, 1592, 1500, 1451, 1516, 1326, 1246, 1139, 1025, 840.	$C_{27}H_{24}N_6O_2S$ 496
3B-d	234 (MeOH)	72 (violet)	510 17,600	3269, 2981, 1645, 1584, 1495, 1446, 1414, 1360, 1259, 1204, 1145, 1104.	$C_{26}H_{21}N_7O_3S$ 511
3B-e	193 (MeOH)	83 (red)	471 29,200	3265, 3065, 1642, 1593, 1562, 1496, 1448, 1404, 1328, 1263, 1147, 1067.	$C_{26}H_{21}BrN_6OS$ 545

Table 3
Characterization data of the compounds **4A**

Dye	M.p./°C (solvent)	Yield/% (color)	UV, λ_{max} (MeOH)/nm ε/l mol^{-1} cm^{-1}	IR (KBr)/cm^{-1}	Mol. formula Mol. wt.
4A-a	197–198 (EtOH)	72 (red)	460 22,300	3064, 1587, 1515, 1495, 1475, 1449, 1375, 1327, 1304, 1285, 1237, 1129.	$C_{27}H_{20}N_4S$ 432
4A-b	176–177 (EtOH)	74 (red)	464 25,200	3063, 1588, 1515, 1490, 1446, 1379, 1332, 1309, 1241, 1132, 1073, 817.	$C_{28}H_{22}N_4S$ 446
4A-c	208–209 (A)	83 (red)	472 27,300	3062, 1599, 1581, 1516, 1500, 1479, 1477, 1329, 1245, 1181, 1130, 1031.	$C_{28}H_{22}N_4OS$ 462
4A-d	199–200 (A)	78 (violet)	510 25,100	3060, 1590, 1510, 1489, 1448, 1342, 1308, 1180, 1108, 1073, 853, 750.	$C_{27}H_{19}N_5O_2S$ 477
4A-e	195–196 (EtOH)	80 (red)	474 26,800	3061, 1587, 1510, 1489, 1447, 1329, 1310, 1130, 1070, 1029, 1011, 970.	$C_{27}H_{19}BrN_4S$ 511

(A) = EtOH + DMF.

Table 4
Characterization data of the compounds **4B**

Dye	M.p./°C (solvent)	Yield /% (color)	UV, λ_{max} (MeOH)/nm ϵ/l mol^{-1} cm^{-1}	IR (KBr)/cm^{-1}	Mol. Formula	HRMS-C HRMS-F
4B-a	227–228 (MeOH)	78 (red)	463 24,000	3071, 1662, 1590, 1516, 1475, 1447, 1320, 1237.	$C_{32}H_{26}N_6OS$	542.1888 542.1889
4B-b	267–268 (MeOH)	85 (red)	465 25,100	3061, 1661, 1592, 1517, 1479, 1453, 1323, 1220.	$C_{33}H_{28}N_6OS$	556.2045 556.2026
4B-c	244–245 (MeOH)	92 (red)	469 28,000	3062, 1677, 1592, 1477, 1448, 1411, 1342, 1250.	$C_{33}H_{28}N_6O_2S$	572.1994 572.1993
4B-d	261–262 (MeOH)	83 (violet)	521 26,500	3061, 1669, 1589, 1515, 1476, 1448, 1407, 1314.	$C_{32}H_{25}N_7O_3S$	587.1739 587.1741
4B-e	257–258 (MeOH)	74 (red)	475 27,900	3066, 1669, 1593, 1520, 1474, 1447, 1403, 1316.	$C_{32}H_{25}BrN_6OS$	620.0994 620.0998

HRMS-C: High Resolution Mass Spectrum—Calculated. HRMS-F: High Resolution Mass Spectrum—Found (EI).

Table 5
Characterization data of the compounds **6A**

Dye	M.p./°C (solvent)	Yield /% (color)	UV, λ_{max} (MeOH)/nm ϵ/l mol^{-1} cm^{-1}	IR (KBr)/cm^{-1}	Mol. formula Mol. wt.
6A-a	201 (EtOH)	64 (yellow)	410 17,200	3146, 2948, 1698, 1530, 1480, 1435, 1403, 1335, 1303, 1283, 1241, 1116.	$C_{17}H_{13}ClN_4OS$ 356.5
6A-b	206 (EtOH)	73 (red)	413 18,800	3386, 2958, 1689, 1598, 1579, 1533, 1485, 1446, 1398, 1325, 1285, 1204.	$C_{18}H_{15}ClN_4OS$ 370.5
6A-c	187 (EtOH)	83 (red)	420 19,300	3393, 2948, 1688, 1598, 1579, 1537, 1484, 1328, 1287, 1251, 1132, 1036.	$C_{18}H_{15}ClN_4O_2S$ 386.5
6A-d	256 (A)	82 (violet)	455 17,500	3272, 2942, 1725, 1585, 1537, 1474, 1366, 1321, 1289, 1244, 1194, 1105.	$C_{17}H_{12}ClN_5O_3S$ 401.5
6A-e	242 (A)	79 (red)	418 18,900	3180, 2939, 1699, 1646, 1588, 1517, 1471, 1445, 1412, 1379, 1326, 1277.	$C_{17}H_{12}BrClN_4OS$ 435.5

(A) = EtOH + DMF.

Table 6
Characterization data of the compounds **6B**

Dye	M.p./°C (solvent)	Yield /% (color)	UV, λ_{max} (MeOH)/nm ϵ/l mol^{-1} cm^{-1}	IR (KBr)/cm^{-1}	Mol. Formula	HRMS-C HRMS-F
6B-a	229 (EtOH)	79 (orange)	416 17,800	3104, 1707, 1626, 1590, 1539, 1497, 1424, 1321.	$C_{22}H_{19}ClN_6O_2S$	466.0978 466.0945
6B-b	222 (EtOH)	77 (orange)	418 19,100	3120, 1695, 1625, 1590, 1551, 1495, 1415, 1320.	$C_{23}H_{21}ClN_6O_2S$	480.1135 480.1147
6B-c	178 (EtOH)	74 (brown)	422 19,700	3148, 1705, 1635, 1600, 1581, 1496, 1416, 1326.	$C_{23}H_{21}ClN_6O_3S$	496.1084 496.1105
6B-d	216 (DMF)	82 (brown)	468 17,500	3147, 1699, 1631, 1589, 1516, 1414, 1332, 1187.	$C_{22}H_{18}ClN_7O_4S$	511.0829 511.0802
6B-e	243 (EtOH)	85 (orange)	425 19,400	3123, 1702, 1632, 1590, 1545, 1494, 1410, 1335.	$C_{22}H_{18}BrClN_6O_2S$	546.0064 546.0056

HRMS-C: High Resolution Mass Spectrum—Calculated. HRMS-F: High Resolution Mass Spectrum—Found (EI).

Table 7
Characterization data of the compounds **7A**

Dye	M.p./°C (solvent)	Yield/% (color)	UV, λ_{max} (MeOH)/nm	IR (KBr)/cm^{-1}	Mol. formula Mol. wt.
7A-a	241 (A)	81 (orange)	411	3148, 2954, 1684, 1559, 1519, 1480, 1455, 1429, 1393, 1327, 1285, 1238.	$C_{24}H_{17}N_5OS_3$ 487
7A-b	239 (A)	89 (orange)	414	3165, 2912, 1690, 1641, 1586, 1522, 1485, 1430, 1386, 1326, 1240, 1172.	$C_{25}H_{19}N_5OS_3$ 501
7A-c	226 (A)	87 (orange)	420	3172, 2969, 1683, 1600, 1580, 1552, 1485, 1428, 1330, 1249, 1182, 1140.	$C_{25}H_{19}N_5O_2S_3$ 517
7A-d	262 (A)	78 (red)	447	3275, 2952, 1695, 1604, 1520, 1473, 1427, 1368, 1320, 1286, 1245, 1187.	$C_{24}H_{16}N_6O_3S_3$ 532
7A-e	250 (A)	82 (red)	419	3163, 2941, 1686, 1568, 1519, 1455, 1429, 1381, 1321, 1287, 1243, 1125.	$C_{24}H_{16}BrN_5OS_3$ 565

(A) = (EtOH + DMF).

Table 8
Characterization data of the compounds **7B**

Dye	M.p./°C (solvent)	Yield/% (color)	UV, λ_{max} (MeOH)/nm	IR (KBr)/cm^{-1}	Mol. formula Mol. wt
7B-a	155–156 (EtOH)	76 (red)	411	3170, 2922, 1699, 1641, 1588, 1544, 1495, 1456, 1426, 1310, 1241, 1124.	$C_{29}H_{23}N_7O_2S_3$ 597
7B-b	164–165 (EtOH)	72 (red)	413	3163, 2930, 1700, 1636, 1591, 1545, 1496, 1456, 1427, 1312, 1242, 1128.	$C_{30}H_{25}N_7O_2S_3$ 611
7B-c	160–161 (EtOH)	58 (orange)	418	3171, 2938, 1699, 1632, 1597, 1558, 1497, 1428, 1316, 1249, 1146, 1024.	$C_{30}H_{25}N_7O_3S_3$ 627
7B-d	233–234 (EtOH)	82 (violet)	472	3170, 2935, 1693, 1626, 1553, 1514, 1428, 1314, 1146, 1105, 1005, 859.	$C_{29}H_{22}N_8O_4S_3$ 642
7B-e	122–123 (EtOH)	78 (orange)	422	3160, 2939, 1695, 1641, 1590, 1559, 1489, 1455, 1425, 1311, 1121, 1079.	$C_{29}H_{22}BrN_7O_2S_3$ 676

component (e.g. dyes **3A-d**, **6A-d**, **6B-d**). The nitro group increases the polarity of the dyes which may link them more strongly to the fabric and it opens an extra way for the energy dissipation after light absorption which decreases the chances for photobleaching.

2.5.2. Color assessment

The color of the dyed fabric was assessed by tristimulus colorimetry. The results are listed in the Tables 12 and 13. It was observed that

1. the color hues of the dyes **3, 4, 6** and **7** on polyester fabric are shifted to the reddish and yellowish directions on the red-green and yellow-blue axes, respectively;
2. the 2-amino-4-antipyrinyl-thiazole dyes **3B, 4B, 6B, 7B** are lighter than the corresponding 2-amino-4-phenyl-thiazole dyes **3A, 4A, 6A, 7A** according to the color lightness values (L^*);
3. the 2-amino-4-phenyl-thiazole dyes **3A–4A** are brighter than the corresponding 2-amino-4-antipyrinyl-thiazole dyes **3B–4B** according to the color brightness values (C^*).

3. Experimental

All melting points are uncorrected. IR spectra (KBr) were recorded with a Perkin-Elmer 1720-X. Elemental analyses were carried out at the Microanalytical Unit of the Faculty of Science, Mansoura University, Egypt using a Perkin-Elmer 2400 CHN Microanalyser. The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker WP 300, UV/Vis spectra with a Perkin-Elmer Lambda 551 S spectrometer and mass spectra with a Finnigan MAT 212 instrument. B3LYP (basis set 6-31G*) density functional theory calculations with full geometry optimization were performed with the program TITAN, version 1.01, of Wavefunction, Inc., Irvine, USA. Solvation energies

(aqueous) were calculated on the basis of the B3LYP results using the semiempiric SM5.4/A routine.

3.1. Synthesis of 2-amino-5-(arylazo)thiazoles (**3** and **4**)

A solution of sodium nitrite (0.70 g in 10 ml water) was gradually added to a well-cooled solution of the aromatic amine (0.010 mol) in conc. HCl (3.0 ml). The diazonium salt solution was added with continuous stirring to an ice cooled solution of the 2-aminothiazole derivative **1** or **2** in pyridine (50 ml). The reaction mixture was allowed to stand for 2 h and then filtered. The 2-amino-5-arylazothiazoles thus obtained, were dried and recrystallized from the appropriate solvent (Tables 1–4).

3A-a, ^{1}H NMR ($CDCl_3$): δ/ppm = 7.10–7.45 (m, 11H, Ar–H), 7.75 (ψ d, 2H, Ar–H), 8.25 (ψd, 2H, Ar–H), 8.65 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 120.25 (2C), 122.54 (2C), 124.72, 128.32 (2C), 129.03 (2C), 129.49 (4C), 130.28 (2C), 133.73, 138.83, 140.89, 152.76, 153.75, 166.26; HRMS: Calcd for $C_{21}H_{16}N_4S$ 356.1095, Found: 356.1096.

3A-b, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.40 (s, 3H, CH_3), 7.05–7.45 (m, 10H, Ar–H), 7.65 (ψd, 2H, Ar–H), 8.25 (ψd, 2H, Ar–H), 8.45 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 21.40, 119.93 (2C), 122.52 (2C), 124.50, 128.31 (2C), 129.32, 129.50 (2C), 129.74 (2C), 130.24 (2C), 133.86, 138.84, 140.01, 141.11, 150.85, 152.89, 165.53; HRMS: Calcd for $C_{22}H_{18}N_4S$ 370.1252, Found: 370.1254.

3A-c, ^{1}H NMR ($CDCl_3$/DMSO): δ/ppm = 3.85 (s, 3H, CH_3), 6.95 (ψd, 2H, Ar–H), 7.05 (ψt, 1H, Ar–H), 7.30–7.80 (m, 9H, Ar–H), 8.35 (ψd, 2H, Ar–H), 10.50 (s, 1H, NH); ^{13}C NMR ($CDCl_3$/DMSO): δ/ppm = 54.17, 113.11 (2C), 117.55 (2C), 121.65, 122.60 (2C), 126.97 (2C), 127.71 (3C), 128.76 (2C), 132.90, 138.88, 139.83, 145.62, 150.76, 159.46, 162.30.

3A-d, MS (EI): m/z (%) = 401 (M, 100), 354, 326, 251, 207, 148, 133, 104, 89, 77.

3A-e, HRMS: Calcd for $C_{21}H_{15}BrN_4S$ 434.0201, Found: 434.0207.

3B-a, ^{1}H NMR (DMSO-d_6): δ/ppm = 2.35 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.05–7.70 (m, 15H, Ar–H), 10.75 (s, 1H, NH); ^{13}C NMR (CF_3COOD): δ/ppm = 12.96, 33.73, 95.59, 122.29 (2C), 123.02 (2C), 128.60 (2C), 129.55 (2C), 129.73 (2C), 130.66 (2C), 130.73 (2C), 132.28, 132.38 (2C), 135.55, 136.56, 149.00, 149.45, 159.60, 168.75; MS (EI): m/z (%) = 466 (M), 438 (100), 421, 374, 362, 345, 318, 243, 219, 169, 93, 77, 56.

3B-b, ^{1}H NMR (DMSO-d_6): δ/ppm = 2.35 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.00–7.70 (m, 14H, Ar–H), 10.70 (s, 1H, NH); ^{13}C NMR (DMSO): δ/ppm = 18.03, 26.58, 40.55, 109.53, 124.31 (2C), 127.12 (2C), 128.31, 130.33 (2C), 132.33, 134.26 (2C), 134.44 (2C), 134.92 (2C), 140.33, 144.43, 145.43, 145.77, 153.17, 156.06, 159.94, 168.43, 169.87; MS (EI): m/z (%) = 480 (M, 100), 451, 388, 362, 332, 269, 243, 226, 214, 197, 135, 106, 91, 77, 56.

3B-c, ^{1}H NMR (CF_3COOD): δ/ppm = 2.75 (s, 3H, CH_3), 3.60 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 7.00 (ψd, 2H, Ar–H), 7.40–7.75 (m, 12H, Ar–H); ^{13}C NMR (CF_3COOD): δ/ppm = 12.75, 33.67, 55.81, 95.23, 115.10 (2C), 123.04 (2C), 125.26 (2C), 128.55 (2C), 129.36 (2C), 129.88, 130.65 (2C), 130.70 (2C), 132.31, 135.65, 137.37, 145.05, 148.48, 159.34, 163.48, 167.66; MS (EI): m/z (%) = 496 (M), 468 (100), 404, 373, 362, 348, 243, 214, 136, 107, 77, 56.

3B-d, ^{1}H NMR (CF_3COOD): δ/ppm = 2.90 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 7.45–7.80 (m, 12H, Ar–H), 7.35 (ψd, 2H, Ar–H); MS (EI): m/z (%) = 511 (M, 100), 483, 419, 391, 373, 345, 243, 214, 121, 77, 56.

3B-e, ^{1}H NMR (DMSO-d_6): δ/ppm = 2.50 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.05-7.70 (m, 14H, Ar–H), 10.70 (s, 1H, NH); MS (EI): m/z (%) = 546 (M + 2), 544 (M), 518, 516 (100), 454, 452, 425, 423, 373, 362, 329, 243, 218, 171, 135, 93, 77, 56.

4A-a, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 7.30–7.55 (m, 16H, Ar–H), 7.65 (ψd, 2H, Ar–H), 8.15 (ψd, 2H, Ar–H).

4A-b, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 2.40 (s, 3H, CH_3), 7.05 (ψd, 2H, Ar–H), 7.25-7.65 (m, 17H, Ar–H).

4A-c, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 3.85 (s, 3H, CH_3), 6.95 (ψd, 2H, Ar–H), 7.35-7.55 (m, 13H, Ar–H), 7.65 (ψd, 2H, Ar–H), 8.00 (ψd, 2H, Ar–H).

4A-d, ^{1}H NMR ($CDCl_3/CF_3COOD$): δ/ppm = 7.20-7.55 (m, 17H, Ar–H), 8.05 (ψd, 2H, Ar–H).

4A-e, ^{1}H NMR ($CDCl_3/CF_3COOD$): δ/ppm = 7.10-7.60 (m, Ar–H).

4B-a, ^{1}H NMR (CF_3COOD): δ/ppm = 2.80 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 7.35–7.90 (m, 20H, Ar–H); MS (EI): m/z (%) = 542 (M, 100), 450, 394, 345, 336, 243, 212, 77, 56.

4B-b, ^{1}H NMR (CF_3COOD): δ/ppm = 2.40 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 7.25-7.90 (m, 19H, Ar–H); MS (EI): m/z (%) = 556 (M, 100), 464, 408, 345, 336, 243, 212, 56.

4B-c, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.35 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.85 (ψd, 2H, Ar–H), 7.20–7.50 (m, 15H, Ar–H), 7.65 (ψd, 2H, Ar–H); ^{13}C NMR ($CDCl_3$): δ/ppm = 12.69, 35.35, 55.42, 105.43, 114.14 (2C), 123.77 (2C), 124.88 (2C), 126.48 (4C), 126.70 (2C), 126.82 (2C), 129.13 (2C), 129.57 (4C), 135.17, 143.05, 144.01, 146.59, 147.33, 154.64, 160.72, 163.24, 168.36; MS (EI): m/z (%) = 572 (M, 100), 544, 480, 438, 424, 410, 345, 304, 243, 212, 77, 56.

4B-d, ^{1}H NMR (CF_3COOD): δ/ppm = 2.80 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 7.45 (ψd, 2H, Ar–H), 7.50–7.80 (m, 15H, Ar–H), 8.35 (ψd, 2H, Ar–H); MS (EI): m/z (%) = 587 (M, 100), 495, 449, 336, 243, 212, 56.

4B-e, ^{1}H NMR (CF_3COOD): δ/ppm = 2.80 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 7.45 (ψd, 2H, Ar–H), 7.50-7.85 (m, 17H, Ar–H); MS (EI): m/z (%) = 622 (M + 2, 100), 620 (M, 96), 530, 528, 437, 336, 243, 212, 77, 56.

*3.2. Synthesis of 2-chloroacetylamino-5-arylazothiazoles (**6**)*

To a solution of the 2-amino-5-(arylazo)thiazole **5** (3.00 mmol) in DMF (15 ml) containing triethylamine (0.5 ml), chloroacetyl chloride (0.50 ml, 6.0 mmol) was added dropwise with stirring at room temperature. Stirring was continued for 4 h and the reaction mixture was poured into ice cooled water. The resuling precipitate was collected, dried and recrystallized (Tables 5 and 6).

6A-a, ^{1}H NMR ($CDCl_3$): δ/ppm = 4.10 (s, 2H, CH_2), 7.35–7.55 (m, 6H, Ar–H), 7.80 (ψd, 2H, Ar–H), 8.25 (ψd, 2H, Ar–H), 10.15 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 41.97, 123.07 (2C), 128.58 (2C), 129.17 (2C), 129.51, 130.02 (2C), 130.83, 133.51, 145.94, 150.32, 152.43, 157.69, 164.33; MS (EI): m/z (%) = 356 (M, 100), 320, 279, 251, 210, 174, 147, 133, 89, 77.

6A-b, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.40 (s, 3H, CH_3), 4.10 (s, 2H, CH_2), 7.25 (ψd, 2H, Ar–H), 7.35-7.50 (m, 3H, Ar–H), 7.70 (ψd, 2H, Ar–H), 8.20 (ψd, 2H, Ar–H), 10.10 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 21.96, 42.39, 123.48 (2C), 128.98 (2C), 129.80, 130.29 (2C), 130.39 (2C), 134.03, 141.96, 146.52, 150.00, 151.00, 157.75, 164.68; HRMS: Calcd. for $C_{18}H_{15}ClN_4OS$ 370.0655, Found: 370.0655.

6A-c, ^{1}H NMR ($CDCl_3$): δ/ppm = 3.85 (s, 3H, CH_3), 4.10 (s, 2H, CH_2), 7.00 (ψd, 2H, Ar–H), 7.40-7.55 (m, 3H, Ar–H), 7.80 (ψd, 2H, Ar–H), 8.20 (ψd, 2H, Ar–H), 10.05 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 41.97, 55.57, 114.41 (2C), 124.92 (2C), 128.50 (2C), 129.19, 129.84 (2C), 133.68, 146.25, 146.84, 148.67, 156.75, 162.00, 164.14).

6B-a, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.40 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 4.30 (s, 2H, CH_2), 7.35–7.55 (m, 8H, Ar–H), 7.75 (ψd, 2H, Ar–H), 12.70 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 11.51, 34.10, 41.19, 102.43, 121.19 (2C), 124.07 (2C), 126.13, 128.01 (2C), 128.08 (2C), 129.19, 133.75, 143.71, 144.35, 151.31, 153.20, 158.06, 161.91, 164.47; MS (EI): m/z (%) = 466 (M), 430, 385, 362, 313, 286, 240, 169, 112, 93 (100), 77.

6B-b, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.40 (s, 6H, $2CH_3$), 3.30 (s, 3H, CH_3), 4.35 (s, 2H, CH_2), 7.25 (ψd, 2H, Ar–H), 7.30–7.50 (m, 5H, Ar–H), 7.70 (ψd, 2H, Ar–H), 12.75 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 10.86, 19.67, 33.64, 40.72, 101.67, 120.63 (2C), 123.29 (2C), 125.32, 127.48 (2C), 128.16 (2C), 133.47, 138.96, 142.84, 143.41, 148.85, 153.03, 156.99, 161.30, 163.95; MS (EI): m/z (%) = 480 (M), 444, 362, 330, 286, 253, 240, 183, 126, 107 (100), 91, 77.

6B-c, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.35 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 6.95 (ψd, 2H, Ar–H), 7.25–7.45 (m, 5H, Ar–H), 7.75 (ψd, 2H, Ar–H), 12.70 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 12.63, 35.10, 42.54, 55.55, 103.78, 114.29 (2C), 124.31 (2C), 125.63 (2C), 127.73, 129.31 (2C), 134.20, 142.56, 145.86,

146.89, 153.77, 158.33, 161.69, 163.24, 165.42; MS (EI): m/z (%) = 496 (M), 477 (100), 451, 380, 302, 279, 266, 197, 148, 105.

6B-d, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.35 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 7.30–7.50 (m, 5H, Ar–H), 7.80 (ψd, 2H, Ar–H), 8.25 (ψd, 2H, Ar–H), 12.45 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 12.61, 34.78, 42.52, 102.95, 122.72 (2C), 124.74 (2C), 126.21 (2C), 128.41, 129.50 (2C), 133.72, 145.22, 147.77, 148.34, 152.96, 156.03, 160.92, 162.84, 165.86; MS (EI): m/z (%) = 511 (M), 493 (100), 460, 420, 380, 346, 312, 299, 286, 266, 214, 197, 148, 108, 77.

6B-e, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 2.90 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 4.40 (s, 2H, CH_2), 7.45 (ψd, 2H, Ar–H), 7.55 (ψd, 2H, Ar–H), 7.60–7.80 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$/CF_3COOD): δ/ppm = 13.08, 33.72, 41.53, 98.49, 124.39 (2C), 128.23, 128.45 (2C), 129.21, 131.06 (2C), 133.04, 133.39 (2C), 139.46, 143.77, 149.14, 149.51, 156.76, 159.74, 167.27; MS (EI): m/z (%) = 546 (^{81}Br, M^+), 544 (^{79}Br, M^+), 493 (100), 491, 477, 475, 402, 380, 279, 266, 197, 148.

3.3. Reaction of **6** with 2-mercaptobenzothiazole (synthesis of 7)

A mixture of the 2-chloroacetylamino-5-(arylazo)thiazole **6** (3.00 mmol) and 2-mercaptobenzothiazole (501 mg, 3.00 mmol) was refluxed for 3 h in ethanol (50 ml) containing 5 drops of triethylamine. The solid product that separated on cooling was filtered off and crystallized (Tables 7 and 8).

7A-a, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 4.70 (s, 2H, CH_2), 7.50–8.00 (m, 14H, Ar–H); ^{13}C NMR ($CDCl_3$/CF_3COOD): δ/ppm = 38.35, 117.84, 122.31, 123.79 (2C), 126.31, 128.46, 129.43 (2C), 129.52 (2C), 129.62 (2C), 130.15 (2C), 132.05, 133.39, 140.16, 142.08, 142.86, 151.16, 162.25, 165.64, 174.84; HRMS: Calcd. for $C_{24}H_{17}N_5OS_3$ 487.0595, Found: 487.0607.

7A-b, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 2.40 (s, 3H, CH_3), 4.55 (s, 2H, CH_2), 7.30 (ψd, 2H, Ar–H), 7.45–7.60 (m, 5H, Ar–H), 7.70 (ψd, 2H, Ar–H), 7.85 (ψd, 1H, Ar–H), 7.95 (m, 3H, Ar–H); ^{13}C NMR ($CDCl_3$/CF_3COOD): δ/ppm = 21.57, 38.44, 117.67, 122.45, 123.08, 123.90 (2C), 126.40, 128.66, 129.40 (2C), 129.55 (2C), 130.12, 130.42 (2C), 132.03, 139.57, 141.75, 143.25, 145.14, 149.33, 162.08, 165.65, 175.29; HRMS: Calcd. for $C_{25}H_{19}N_5OS_3$ 501.0751, Found: 501.0755.

7A-c, ^{1}H NMR ($CDCl_3$/CF_3COOD): δ/ppm = 3.95 (s, 3H, CH_3), 4.70 (s, 2H, CH_2), 7.05 (ψd, 2H, Ar–H), 7.55–8.05 (m, 11H, Ar–H); ^{13}C NMR (CF_3COOD): δ/ppm = 38.58, 55.93, 115.29 (2C), 120.24, 122.64, 125.53, 126.41 (2C), 129.03, 129.33 (2C), 129.67 (2C), 129.94, 130.75, 132.16, 138.92, 141.13, 143.64, 145.76, 161.74, 164.13, 165.72, 176.05; HRMS: Calcd. for $C_{25}H_{19}N_5O_2S_3$ 517.0700, Found: 517.0690.

7A-d, MS (EI): m/z (%) = 532 (M), 352, 324, 278, 208 (100), 180, 167, 133, 89.

7A-e, MS (EI): m/z (%) = 566 (M + 2), 564 (M), 358, 356, 282, 208 (100), 167, 133, 89, 77.

7B-a, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.30 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 7.20–7.50 (m, 11H, Ar–H), 7.65 (ψd, 2H, Ar–H), 7.85 (ψd, 1H, Ar–H), 12.20 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 12.59, 34.94, 36.81, 103.74, 121.01, 121.69, 122.41 (2C), 124.47, 125.81 (2C), 126.14, 127.75, 128.94 (2C), 129.31 (2C), 130.18, 134.20, 135.39, 144.75, 145.55, 152.45, 152.55, 153.68, 159.37, 163.21, 165.69, 166.64; MS (EI): m/z (%) = 597 (M), 492, 390, 362, 313, 286, 242, 207, 167 (100), 108, 77, 56.

7B-b, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 7.10 (ψd, 2H, Ar–H), 7.20–7.70 (m, 10H, Ar–H), 7.85 (ψd, 1H, Ar–H), 12.10 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 12.58, 21.43, 34.97, 36.80, 103.81, 120.96, 121.68, 122.36 (2C), 124.42, 125.73 (2C), 126.10, 127.66, 129.27 (2C), 129.60 (2C), 134.24, 135.38, 140.75, 143.93, 145.68, 150.54, 152.56, 153.75, 159.03, 163.26, 165.67, 166.54; MS (EI): m/z (%) = 611 (M), 492, 419, 404, 376, 313 (100), 286, 208, 167, 106, 91.

7B-c, ^{1}H NMR ($CDCl_3$): δ/ppm = 2.25 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 6.80 (ψd, 2H, Ar–H), 7.20–7.50 (m, 8H, Ar–H), 7.65 (ψd, 2H, Ar–H), 7.85 (ψd, 1H, Ar–H), 12.10 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ/ppm = 12.57, 35.01, 36.76, 55.46, 104.04, 114.17 (2C), 120.97, 121.71, 124.20 (2C), 124.47, 124.90, 125.67 (2C), 126.13, 127.59, 129.25 (2C), 134.43, 135.41, 142.94, 144.83, 146.93, 152.56, 153.86,

161.50, 163.51, 165.64, 166.43; MS (EI): m/z (%) = 492 ($M-C_7H_7N_2O$), 420, 392, 313, 286 (100), 214, 167, 108.

7B-d, ^{1}H NMR ($CDCl_3/CF_3COOD$): δ/ppm = 2.95 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 4.65 (s, 2H, CH_2), 7.45 (ψd, 2H, Ar–H), 7.65–7.85 (m, 7H, Ar–H), 8.00 (ψd, 2H, Ar–H), 8.35 (ψd, 2H, Ar–H); MS (EI): m/z (%) = 642 (M), 492, 435, 391, 314, 271, 240, 180, 167 (100), 138, 108, 65.

7B-e, ^{1}H-NMR ($CDCl_3$): δ/ppm = 2.65 (s, 3H, CH_3), 3.15 (s, 3H, CH_3), 4.15 (s, 2H, CH_2), 7.20–7.85 (m, 12H, Ar–H), 8.05 (ψd, 1H, Ar–H), 12.05 (s, 1H, NH); MS (EI): m/z (%) = 492 ($M-C_6H_4BrN_2$), 419, 313 (100), 286, 243, 208, 167, 108, 77.

Table 9
Elemental analysis data

Dye	Molecular formula	C Calcd. (Found)	H Calcd. (Found)	N Calcd. (Found)
3A-a	$C_{21}H_{16}N_4S$	70.76 (70.78)	4.52 (4.62)	15.72 (15.84)
3A-b	$C_{22}H_{18}N_4S$	71.32 (71.42)	4.90 (5.12)	15.12 (15.10)
3A-c	$C_{22}H_{18}N_4O_2S$	68.37 (68.38)	4.69 (4.57)	14.50 (14.43)
3A-d	$C_{21}H_{15}N_5O_2S$	62.83 (62.91)	3.77 (3.67)	17.45 (17.32)
3A-e	$C_{21}H_{15}BrN_4S$	57.94 (57.81)	3.47 (3.59)	12.87 (12.94)
3B-a	$C_{26}H_{22}N_6OS$	66.93 (66.94)	4.75 (4.66)	18.01 (18.11)
3B-b	$C_{27}H_{24}N_6OS$	67.48 (67.44)	5.03 (5.06)	14.49 (14.62)
3B-c	$C_{27}H_{24}N_6O_2S$	65.30 (65.43)	4.87 (4.77)	16.92 (16.81)
3B-d	$C_{26}H_{21}N_7O_3S$	61.04 (61.10)	4.14 (4.11)	19.17 (19.22)
3B-e	$C_{26}H_{21}BrN_6OS$	57.25 (57.37)	3.88 (4.03)	15.41 (15.33)
4A-a	$C_{27}H_{20}N_4S$	74.97 (75.09)	4.66 (4.78)	12.95 (12.81)
4A-b	$C_{28}H_{22}N_4S$	75.31 (75.25)	4.97 (5.03)	12.55 (12.44)
4A-c	$C_{28}H_{22}N_4OS$	72.70 (72.61)	4.79 (4.64)	12.11 (12.08)
4A-d	$C_{27}H_{19}N_5O_2S$	67.91 (67.78)	4.01 (3.88)	14.67 (14.52)
4A-e	$C_{27}H_{19}BrN_4S$	63.41 (63.32)	3.74 (3.75)	10.95 (11.01)
4B-a	$C_{32}H_{26}N_6OS$	70.83 (70.79)	4.83 (4.85)	15.49 (15.53)
4B-b	$C_{33}H_{28}N_6OS$	71.20 (71.25)	5.07 (5.10)	15.10 (15.17)
4B-c	$C_{33}H_{28}N_6O_2S$	69.21 (69.23)	4.93 (4.93)	14.67 (14.72)
4B-d	$C_{32}H_{25}N_7O_3S$	65.40 (65.53)	4.29 (4.32)	16.68 (16.51)
4B-e	$C_{32}H_{25}BrN_6OS$	61.84 (61.91)	4.05 (4.09)	13.52 (13.63)
6A-a	$C_{17}H_{13}ClN_4OS$	57.22 (57.42)	3.67 (3.76)	15.70 (15.62)
6A-b	$C_{18}H_{15}ClN_4OS$	58.30 (58.37)	4.08 (4.09)	15.11 (15.23)
6A-c	$C_{18}H_{15}ClN_4O_2S$	55.88 (55.93)	3.91 (4.03)	14.48 (14.47)
6A-d	$C_{17}H_{12}ClN_5O_3S$	50.81 (50.81)	3.01 (3.09)	17.43 (17.56)
6A-e	$C_{17}H_{12}$ $BrClN_4OS$	46.86 (46.68)	2.78 (2.63)	12.86 (12.71)
6B-a	$C_{22}H_{19}ClN_6O_2S$	56.59 (56.56)	4.10 (4.11)	18.00 (17.86)
6B-b	$C_{23}H_{21}ClN_6O_2S$	57.44 (57.56)	4.40 (4.46)	17.47 (17.53)
6B-c	$C_{23}H_{21}ClN_6O_3S$	55.59 (55.63)	4.26 (4.33)	16.91 (16.82)
6B-d	$C_{22}H_{18}ClN_7O_4S$	51.61 (51.40)	3.54 (3.66)	19.15 (19.32)
6B-e	$C_{22}H_{18}BrClN_6O_2S$	48.41 (48.58)	3.32 (3.52)	15.40 (15.58)
7A-a	$C_{24}H_{17}N_5OS_3$	59.12 (59.37)	3.51 (3.61)	14.36 (14.47)
7A-b	$C_{25}H_{19}N_5OS_3$	59.86 (59.92)	3.82 (3.80)	13.96 (13.87)
7A-c	$C_{25}H_{19}N_5O_2S_3$	58.01 (57.91)	3.70 (3.66)	13.53 (13.55)
7A-d	$C_{24}H_{16}N_6O_3S_3$	54.12 (53.80)	3.03 (2.89)	15.78 (15.70)
7A-e	$C_{24}H_{16}BrN_5OS_3$	50.88 (50.77)	2.85 (3.01)	12.36 (12.44)
7B-a	$C_{29}H_{23}N_7O_2S_3$	58.27 (58.11)	3.88 (3.81)	16.40 (16.56)
7B-b	$C_{30}H_{25}N_7O_2S_3$	58.90 (58.77)	4.12 (3.98)	16.03 (16.13)
7B-c	$C_{30}H_{25}N_7O_3S_3$	57.40 (57.32)	4.01 (4.10)	15.62 (15.77)
7B-d	$C_{29}H_{22}N_8O_4S_3$	54.19 (54.28)	3.45 (3.62)	17.43 (17.52)
7B-e	$C_{29}H_{22}BrN_7O_2S_3$	51.48 (51.66)	3.28 (3.39)	14.49 (14.62)

3.4. Dyeing and fastness determinations

3.4.1. Dyeing procedure

The fabric was dyed with 2.0% dye (calculated on weight of the fabric), 1% Avolan IS (as a dispersing agent), kept at a liquor ratio of 20:1. The process was started at 60 °C; the temperature was then raised to 130 °C over 30 min and maintained there for 1 h. After cooling, the fabric was taken out and treated with a solution of 2% sodium bisulphite, 2% sodium hydroxide, and 0.1% Avolan IS at 70 °C for 30 min. Finally, the fabric was rinsed and dried at 60 °C.

3.4.2. Color fastness tests

The results are listed in Tables 10 and 11.

3.4.2.1. 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. The staining on the undyed adjacent fabric was assessed according to the following gray scale: 1—poor, 2—fair, 3—moderate, 4—good, 5—excellent.

3.4.2.2. 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 staining on the undyed adjacent fabric was assessed according to the following gray scale: 1—poor, 2—fair, 3—moderate, 4—good, 5—excellent.

The acid solution (pH = 3.5) contains sodium chloride (10 g dm^{-3}), lactic acid (1 g dm^{-3}), disodium orthophosphate (1 g dm^{-3}) and histidine monohydrochloride (0.25 g dm^{-3}). The alkaline solution (pH = 8) contains sodium chloride (10 g dm^{-3}), ammonium chloride (4 g dm^{-3}), disodium orthophosphate (1 g dm^{-3}) and histidine monohydrochloride (0.25 g dm^{-3}).

3.4.2.3. Fastness to rubbing. The dyed polyester fabric was placed on the base of the Crockmeter, so that it rested flatly 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. For

Table 10
Fastness properties of the dyes **3A**, **3B**, **4A** and **4B** on polyester fabric

Dye	Washing	Perspiration		Rubbing		Sublimation fastness			Light (40 h)
		Acid	Alkali	Dry	Wet	Change in tone	Staining at 180 °C	Staining at 210 °C	
3A-a	4–5	4–5	4–5	4–5	4–5	4	4	3–4	5
3A-b	4–5	4	4–5	4	4	4–5	4	3–4	4–5
3A-c	4–5	4–5	4–5	2–3	3	4–5	4–5	4	4–5
3A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	6–7
3A-e	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	7
3B-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4
3B-b	4–5	4–5	4–5	4	4	4–5	4–5	4–5	3–4
3B-c	4–5	4–5	4–5	1–2	2	4–5	4–5	4–5	3–4
3B-d	4–5	4–5	4–5	3–4	3–4	4–5	4–5	4–5	6
3B-e	4–5	4–5	4–5	2	2–3	4–5	4–5	4	5–6
4A-a	4–5	4–5	4–5	4	4	4–5	4–5	4	4–5
4A-b	4–5	4	4	3–4	4	4–5	4	3–4	4
4A-c	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4–5
4A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	6
4A-e	4–5	4–5	4–5	4	4	4–5	4–5	4	4–5
4B-a	4–5	4–5	4–5	3–4	3–4	4–5	4	3–4	4
4B-b	4–5	4	4–5	3	3	4–5	4	4	3–4
4B-c	4–5	4–5	4–5	2–3	3	4	3–4	3	4
4B-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5–6
4B-e	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5

Table 11
Fastness properties of the dyes **6A**, **6B**, **7A** and **7B** on polyester fabric

Dye	Washing	Perspiration		Rubbing		Sublimation fastness			Light (40 h)
		Acid	Alkali	Dry	Wet	Change in tone	Staining at 180 °C	Staining at 210 °C	
6A-a	4–5	4	4–5	3–4	4	4	3–4	3–4	6
6A-b	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	6
6A-c	4–5	4–5	4–5	4	4	4–5	4	3–4	5
6A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	6–7
6A-e	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	6
6B-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5
6B-b	4–5	3–4	4–5	4	4–5	4–5	4–5	4–5	4
6B-c	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	5
6B-d	4–5	4–5	4–5	3	3–4	4–5	4–5	4–5	6–7
6B-e	4–5	4–5	4–5	3–4	4	4–5	4–5	4	5
7A-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5
7A-b	4–5	4	4–5	4	4–5	4–5	4	4	4
7A-c	4–5	4	4–5	4	4–5	4–5	4	3–4	4
7A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5–6
7A-e	4–5	4–5	4–5	4	4	4–5	4	4	5
7B-a	4–5	4–5	4–5	4	4	4–5	4–5	4	4
7B-b	4–5	3–4	4	3–4	4	4–5	4–5	4–5	3–4
7B-c	4–5	4–5	4–5	4	4–5	4–5	4–5	4	3–4
7B-d	4–5	4–5	4–5	3–4	3–4	4–5	4–5	4–5	5
7B-e	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5

Table 12
Color of the dyes **3A**, **3B**, **4A** and **4B** on polyester fabric

Dye	Color coordinates					CIELAB difference				*K*/*S*
	*L**	*a**	*b**	*C**	*H*	Δ*L*	Δ*C*	Δ*H*	Δ*E*	
3A-a	54.93	53.83	65.49	84.77	50.58	–	–	–	–	21.73
3A-b	58.57	54.55	71.32	89.79	52.59	03.64	05.02	03.05	06.91	21.23
3A-c	58.71	52.66	70.29	87.83	53.16	03.78	03.06	03.88	06.22	20.84
3A-d	29.12	42.86	02.83	42.96	03.78	−25.80	−41.81	−47.93	68.64	20.47
3A-e	52.64	58.82	60.28	84.22	45.70	−02.29	−00.55	−07.19	07.56	21.33
3B-a	72.36	28.26	44.61	52.81	57.64	–	–	–	–	02.37
3B-b	60.22	41.37	58.95	72.02	54.94	−12.13	19.21	−02.90	22.91	10.98
3B-c	63.76	33.07	49.32	59.38	56.15	−08.59	06.57	−01.45	10.91	06.06
3B-d	47.23	21.41	−0.74	21.43	−1.98	−25.13	−31.37	−33.45	52.29	02.17
3B-e	52.10	49.39	45.71	67.30	42.78	−20.25	14.49	−15.41	29.29	12.79
4A-a	51.23	55.21	61.28	82.48	47.98	–	–	–	–	20.56
4A-b	54.76	57.44	64.55	86.40	48.33	03.53	03.92	00.55	05.30	21.94
4A-c	52.43	56.73	63.26	84.97	48.11	01.20	02.49	00.17	02.77	20.66
4A-d	27.10	49.64	10.45	50.72	11.89	−24.13	−31.76	−40.07	56.54	22.10
4A-e	52.22	57.88	56.32	80.76	44.22	00.99	−01.72	−05.36	05.72	19.45
4B-a	65.74	36.82	42.27	56.05	48.94	–	–	–	–	05.30
4B-b	58.23	49.41	55.20	74.08	48.16	−07.51	18.03	−00.78	19.54	11.27
4B-c	62.17	43.90	48.45	65.38	47.82	−03.57	09.33	−01.12	10.05	08.36
4B-d	54.12	34.85	40.61	53.51	49.36	−11.62	−02.54	00.43	11.90	06.54
4B-e	51.86	53.10	41.53	67.41	38.03	−13.88	11.36	11.68	21.40	13.68

Table 13
Color of dyes **(6A**, **6B**, **7A** and **7B)** on polyester fabric

Dye	Color coordinates					CIELAB difference				*K*/*S*
	*L**	*a**	*b**	*C**	*H*	Δ*L*	Δ*C*	Δ*H*	Δ*E*	
6A-a	64.34	38.26	77.99	86.87	63.87	–	–	–	–	18.54
6A-b	69.26	34.02	86.92	93.34	68.63	04.92	06.46	07.47	11.04	19.75
6A-c	61.39	40.68	74.45	84.84	61.35	−02.95	−02.03	−03.77	05.20	19.25
6A-d	46.52	48.71	49.44	69.40	45.42	−17.82	−17.46	−24.89	35.24	19.67
6A-e	68.34	38.86	85.71	94.11	65.61	03.99	07.23	02.74	08.71	19.84
6B-a	74.82	17.47	41.92	45.41	67.37	–	–	–	–	01.84
6B-b	83.64	12.28	38.50	40.41	72.31	08.82	−05.00	03.69	10.79	00.91
6B-c	76.02	18.73	51.67	54.96	70.07	01.20	09.54	02.35	09.90	02.60
6B-d	63.51	19.94	14.89	24.89	36.75	−11.31	−20.52	−17.75	29.40	01.25
6B-e	80.66	14.21	26.38	29.97	61.70	05.83	−15.44	−03.65	16.91	00.71
7A-a	81.58	09.47	72.85	73.46	82.60	–	–	–	–	08.18
7A-b	79.73	14.67	83.06	84.34	79.98	−01.84	10.88	−03.59	11.60	12.24
7A-c	77.10	20.57	88.14	90.51	76.86	−04.47	17.04	−08.15	19.42	12.42
7A-d	67.12	33.49	51.42	61.37	56.92	−14.45	−12.09	−29.83	35.28	04.78
7A-e	80.39	11.96	64.90	65.99	79.56	−01.18	−07.46	−03.69	08.41	06.01
7B-a	75.22	22.15	67.86	71.38	71.93	–	–	–	–	05.70
7B-b	71.21	22.73	63.79	67.72	70.39	−04.01	−03.65	−01.86	05.73	05.97
7B-c	66.22	17.72	22.90	28.95	52.26	−09.00	−42.42	−15.52	46.06	01.63
7B-d	65.15	27.56	21.79	35.13	38.32	−10.06	−36.24	−28.95	47.46	01.64
7B-e	75.17	12.22	33.99	36.29	69.48	−00.05	−35.08	−02.17	35.15	01.26

the wet rubbing test, the testing squares were thoroughly immersed in distilled water. The rest of the procedure was the same as in the dry test. The staining on the white testing cloth was assessed according to the gray scale: 1—poor, 2—fair, 3—moderate, 4—good, 5—excellent.

3.4.2.4. Fastness to sublimation. Sublimation fastness was measured with an iron tester (Yasuda N138). 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 °C and 210 °C every 1 min. Any staining on the undyed adjacent fabric or change in tone was assessed according to the following gray scale: 1—poor, 2—fair, 3—moderate, 4—good, 5—excellent.

3.4.2.5. 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. The changes in color were assessed according to the following blue scale: 1—poor, 3—moderate, 5—good, 8—very good.

3.4.3. Color assessment

Tables 12 and 13 report the color parameters of the dyed fabric assessed by tristimulus colorimetry. The color parameters of the dyed fabric were determined on a spectro multichannel photo detector (model MCPD-110A), equipped with a D65 source and barium sulphate as a standard blank. The color of the dyed fabric was assessed in terms of tristimulus colorimetry. The values of the chromaticity coordinates, luminance factor and the positions of colors in the CIELAB color solid are reported.

References

[1] Amishiro N, Nagamuro S, Kobayashi E, Gomi K, Saito H. New water-soluble duocarmycin derivatives: synthesis and antitumor activity of A-ring pyrrole compounds bearing beta-heteroarylacryloyl groups. J Med Chem 1999;42:669–76.

[2] Hattori K, Fujii N, Tanaka A, Takamura, F. Preparation

of 4,5-diaryloxazoles as prostaglandin I2 agonists. WO 99/21843 (Fujisawa Pharmaceutical Co., LTD; C. A. 1999, 130, 325140s).

[3] Cheung M, Glennon KC, Lackey KE, Pell MR. Preparation of arylmethylideneazaoxindoles as protein kinase inhibitors. WO 99/21859 (Glaxo Group LTD; C. A. 1999, 130, 325139y).

[4] Yamaguchi K, Yada M, Tsuji T, Hatanaka Y, Goda K, Kobori T. 4-Phenylthiazole derivatives inhibit IL-6 secretion in osteoblastic cells and suppress bone weight loss in ovariectomized mice. Bioorg Med Chem Lett 1999;9:957–60.

[5] Dhal PN, Nayak A. Spasmolytic activities of aminomethyl derivatives derived from 2-mercaptobenzoxazole and 2-mercaptobenzothiazole. Indian J Pharm 1975;37:92–4.

[6] Ariens EJ, Simonis AM. Aspects of molecular pharmacology. II. Theory of receptors and structure–activity relations. Farmaco, Ediione Scientifica (Pavia) 1966;21:581–608.

[7] Amer FA, Zimaity T, Metwally AM. Synthesis of arylhydrazono-3-(3-pyridyl)-2-pyrazolin-5-ones and 1-aryl-3-(3-pyridyl)-4-arylazo-5-aryliminopyrazoles and their application as disperse dyes. J Appl Chem Biotechnol 1978;28:560–8.

[8] Metwally MA, Amer FA, Ahmed EA, Sadek MK. New azodisperse dyes for dyeing the blend of polyester: wool—part 6. J Text Assoc 2003;63:229–33.

[9] Metwally MA, Abdel-Latif E, Amer FA. New 4-arylazo-2-bromo-2-(α-bromosubstituted)-3-phenyl-1,3-thiazolidin-5-one dyes for dyeing polyester fabrics. J Text Assoc 2002;63:149–54.

[10] Metwally MA, Darwish YM, El-Hussini MM, Amer FA. Synthesis of 4-arylazo-1-phenyl-3-methyl-5-arylaminopyrazole derivatives and their application as disperse dyes. Part-III. J Indian Chem Soc 1988;65:54–9.

[11] Metwally MA, Abdel-Latif E, Amer FA. New 4-arylazo-2-(substituted)-3-phenyl-1,3-thiazolidin-5-ones as disperse dyes (part-1). J Text Assoc 2001;62:155–9.

[12] Shadbolt RS. Tautomeric *N*-substituted 2-phenacylisothiouronium bromides. J Chem Soc 1971;(C):1667–9.

[13] Kaupp G, Schmeyers J, Boy J. Iminium salts in solid-state syntheses giving 100% yield. J Prakt Chem 2000;342:269–80.

[14] Morita M. Synthesis and antibacterial activity of antipyrine derivative. I. 4-Thiazoline-2-thiones, dithiocarbamic acid esters and rhodanines. J Pharm Soc Jp 1962;82:36–45.

[15] Shawali AS, Abdelhamid AO. New routes to aroylthiadiazolines and arylazothiazoles from phenylglyoxalyl bromide arylhydrazones and phenacyl thiocyanate. J Heterocycl Chem 1976;13:45–9.

[16] Mishra V, Jain MC. 2-Amino-4-phenyl-5-phenylazothiazole as an analytical reagent for spectrophotometric determination of iron(III). J Indian Chem Soc 1988;65:883–4.