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New azodisperse dyes with thiazole ring for dyeing polyester fabrics

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Abstract

Diazotized aryl amines were coupled with 2-aminothiazole derivatives to give 5-arylazo-2-aminothiazoles, which on reaction with different reagents such as acetic anhydride and benzoyl chloride yielded the corresponding 2-(N-acetyl-amino)-5-arylazothiazole and 2-(N-benzoyl-amino)-5-arylazothiazole derivatives. These dyes were applied to polyester as disperse dyes and their fastness properties were evaluated. The azo/hydrazo tautomerism of the dyes was judged by density functional calculations at the B3LYP/6-31G* level.

Keywords: Acylation; Antipyrine; Aminothiazole; Azo coupling; Azo/hydrazo tautomerism; Bathochromic and hypsochromic shifts; DFT calculations; Disperse dyes; Fastness properties; Polyester

1. Introduction

Many thiazole ring systems are of considerable importance because of their antibacterial and anti-inflammatory activity [1,2]. Because of the wide spectrum of activity shown by the thiazole moiety, a large number of thiazoles substituted with different groups at various positions have been prepared [3–6]. In this work, we report the synthesis of 5-arylazo-2-thiazolylamines and 5-arylazo-2-thiazolylamides and their application as disperse dyes for dyeing polyester fabrics.

2. Results and discussion

2.1. Coupling of 2-aminothiazoles with aromatic diazonium salts

2-Amino-4-substituted thiazoles **1** [7–9], when coupled with a variety of aromatic diazonium salts in ethanol buffered with sodium acetate, yielded the corresponding 2-amino-5-arylazo-4-substituted-thiazoles **2** and **3** in good yields (Scheme 1; Tables 1–4). Only the compounds **2A-a**–**2A-d** were known [10]. The amino groups are not changed under the experimental conditions. The NH_2-group in **2A**, **B** is clearly indicated by the symmetric and antisymmetric vibrations (IR frequencies at 3270–3460 and 3080–3300 cm^{-1}, Tables 1 and 2), while the NH vibration frequencies of **3A**, **B** are found at 3190-3220 cm^{-1} (Tables 3, 4).

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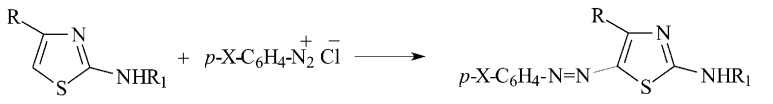


1

a: X = H
b: X = Me
c: X = OMe
d: X = NO_2
e: X = Br

2A: R = Ph, R_1 = H
2B: R = 4-antipyrinyl, R_1 = H
3A: R = Ph, R_1 = Me
3B: R = 4-antipyrinyl, R_1 = Me

Scheme 1. Azo coupling of 2-aminothiazoles at the 5-position.

Further support for the structure of these compounds is obtained by the UV, IR, NMR and mass spectra in the Experimental. All compounds gave rise to the expected signals. The azo-structure of the dyes **2** and **3** (λ_{max} in the range of 424–501 nm) is secured by density functional calculations (B3LYP at the 6-31G* level) that have the hydrazo tautomer higher in energy by 5.3 (**2A-a**), 5.1 (**3A-a**), 4.9 (**3A-d**) kcal mol^{-1}. Thus, it can be safely judged that none of the dyes **1** and **2** accepts the hydrazone structure to a measurable extend. Even the strong π-electron accepting nitro group in **3A-d** does not lead to a change in the tautomeric structure (neither hydrazo- nor *aci*-nitro-tautomer), however the charge separation between the terminal N of the azo-tautomer and the dipole moments vary. The calculated electrostatic charge at the 2-N is −0.756, −0.453 and −0.423, the

Table 1
Characterization data of the compounds **2A**

Cpd. no.	M.p. °C (Solvent)	Lit. m.p. [Ref.]	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula Mol. wt.	HRMS-C / HRMS-F
2A-a	195 (EtOH)	195 [10]	424 (20,000)	3393, 3292, 3061, 2963, 1646, 1528, 1479, 1343, 1305, 1263, 1195, 1148.	$C_{15}H_{12}N_4S$ 280	281.0861 281.0865[a]
2A-b	202 (EtOH)	199 [10]	429 (21,700)	3387, 3273, 3056, 2969, 1645, 1529, 1484, 1325, 1305, 1261, 1210, 1142.	$C_{16}H_{14}N_4S$ 294	295.1017 295.1015[a]
2A-c	207–208 (EtOH)	208 [10]	449 (22,800)	3463, 3271, 3053, 2931, 1635, 1598, 1516, 1485, 1330, 1242, 1142, 1028.	$C_{16}H_{14}N_4OS$ 310	310.0888 310.0886
2A-d	254–255 (DMF)	254 [10]	491 (20,550)	3417, 3298, 3052, 2925, 1649, 1526, 1471, 1333, 1293, 1251, 1193, 1145.	$C_{15}H_{11}N_5O_2S$ 325	325.0634 325.0633
2A-e	256–257 (DMF)	– –	447 (24,000)	3443, 3289, 3060, 2967, 1642, 1523, 1468, 1337, 1293, 1257, 1196, 1139.	$C_{15}H_{11}BrN_4S$ 359	358.9966 358.9971[a]

HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).
[a] M + H; chemical ionization (i-butane).

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

Cpd. no.	M.p. °C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula	HRMS-C / HRMS-F
2B-a	203 (EtOH)	90 (orange)	427 (19,900)	3286, 3146, 1656, 1626, 1592, 1510, 1336, 1270.	$C_{20}H_{18}N_6OS$	390.1263 / 390.1277
2B-b	192 (EtOH)	84 (red)	436 (23,300)	3281, 3121, 1660, 1620, 1592, 1500, 1444, 1337.	$C_{21}H_{20}N_6OS$	404.1419 / 404.1415
2B-c	171 (EtOH)	92 (red)	446 (24,400)	3297, 3160, 1646, 1599, 1499, 1409, 1340, 1248.	$C_{21}H_{20}N_6O_2S$	420.1368 / 420.1367
2B-d	219 (DMF)	87 (green)	495 (20,100)	3268, 3075, 1619, 1588, 1510, 1413, 1317, 1251.	$C_{20}H_{17}N_7O_3S$	435.1113 / 435.1112
2B-e	181 (EtOH)	90 (red)	450 (24,400)	3276, 3150, 1619, 1592, 1500, 1337, 1268, 1194.	$C_{20}H_{17}BrN_6OS$	470.0348 / 470.0348

HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).

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

Cpd. no.	M.p. ° C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula Mol. wt.	HRMS-C / HRMS-F
3A-a	215 (A)	68 (red)	442 (23,800)	3207, 3070, 2911, 1600, 1523, 1479, 1401, 1334, 1292, 1194, 1126, 1051.	$C_{16}H_{14}N_4S$ 294	294.0939 / 294.0939
3A-b	236 (A)	73 (red)	449 (24,000)	3201, 3110, 2915, 1595, 1524, 1483, 1400, 1335, 1292, 1200, 1126, 1050.	$C_{17}H_{16}N_4S$ 308	308.1095 / 308.1094
3A-c	224 (A)	72 (brown)	459 (23,950)	3204, 3110, 2924, 1597, 1524, 1485, 1401, 1335, 1305, 1247, 1201, 1125.	$C_{17}H_{16}N_4OS$ 324	325.1123 / 325.1214[a]
3A-d	278 (DMF)	82 (violet)	497 (25,000)	3194, 3107, 2929, 1590, 1506, 1473, 1401, 1323, 1294, 1260, 1192, 1149.	$C_{16}H_{13}N_5O_2S$ 339	340.0868 / 340.0868[a]
3A-e	255 (A)	76 (red)	462 (24,600)	3202, 3102, 2919, 1593, 1519, 1466, 1399, 1333, 1296, 1195, 1148, 1125.	$C_{16}H_{13}BrN_4S$ 373	372.0044 / 372.0052

(A) = EtOH + DMF. HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).
[a] M + H; chemical ionization (i-butane).

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

Cpd. no.	M.p. °C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula Mol. wt.	HRMS-C / HRMS-F
3B-a	252 (AcOH)	82 (red)	442 (23,800)	3221, 3063, 2999, 1645, 1588, 1567, 1495, 1404, 1316, 1267, 1194, 1150.	$C_{21}H_{20}N_6OS$ 404	404.1419 / 404.1418
3B-b	235 (AcOH)	85 (red)	445 (23,500)	3200, 3101, 2916, 1673, 1587, 1524, 1489, 1401, 1313, 1289, 1197, 1123.	$C_{22}H_{22}N_6OS$ 418	419.1654 / 419.1650[a]
3B-c	176 (AcOH)	78 (brown)	451 (24,450)	3185, 3075, 2937, 1675, 1600, 1580, 1518, 1496, 1398, 1323, 1252, 1025.	$C_{22}H_{22}N_6O_2S$ 434	434.1524 / 434.1514
3B-d	240 (DMF)	80 (violet)	501 (25,100)	3189, 2943, 1646, 1567, 1562, 1500, 1415, 1330, 1253, 1187, 1148, 1101.	$C_{21}H_{19}N_7O_3S$ 449	450.1348 / 450.1342[a]
3B-e	244 (AcOH)	86 (red)	457 (23,900)	3210, 3104, 2923, 1672, 1590, 1519, 1399, 1304, 1279, 1191, 1149, 1123.	$C_{21}H_{19}BrN_6OS$ 483	483.0603[a] / 483.0609[a]

HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).
[a] M + H; chemical ionization (i-butane).

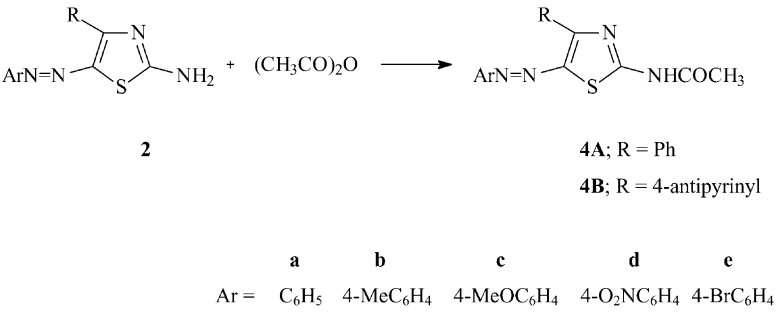
dipole moment 2.20, 2,82 and 10.12 Db in **2A-a**, **3A-a** and **3A-d**, respectively. This compares with the calculated values of −0.689, −0.519, −0.506 and 4.01, 2.89, 4.80 Db of the corresponding hydrazo tautomers. The exothermic energies of solvation (water) change the energetic differences to 7.1, 4.4 and 2.6 kcal mol^{-1} in the systems **2A-a**, **3A-a** and **3A-d**, respectively. Thus, even in the case of the nitro compound 3A-d the hydrazo tautomer is probably not significantly present in solution. It may however appear that it is present in the solid state where polarity plays an important role for the crystal packing [11].

The influence of the antipyrinyl group was also studied by calculation for the system **2B-a**. It turns out that the formulated azo tautomer (μ = 5.68 Db) is 3.2 kcal mol^{-1} more stable than its hydrazo tautomer (μ = 6.58 Db). As the calculated energies of solvation was found 2.6 kcal mol^{-1} more exothermic for the azo tautomer **2B-a** it is clear that the antipyrinyl group in position 3 of the thiazole moiety does not introduce major disturbances to the electronic system when compared to the phenyl group in the same position.

2.2. Reaction of 5-arylazothiazoles **2** with acetic anhydride

A series of 2-(N-acetylamino)-5-arylazothiazoles **4** was synthesized by treatment of the corresponding 2-amino-5-arylazothiazoles **2A**, **2B** with acetic anhydride at 65 °C (Scheme 2). The spectral data of the amides **4A**, **B** are consistent with their structures. Their IR spectra exhibit a broad band around 3165 cm^{-1} (amide NH), a strong sharp band in the region of 1703–1664 cm^{-1} (amide CO) and bands around 1600, 1530, 1480 and 1440 cm^{-1} due to thiazole and phenyl ring vibrations. The ^{1}H-NMR spectra of the sufficiently soluble compounds exhibit all of the required peaks (see Experimental).

As in Ref. [12], the azo tautomer structure of **4** has been secured by density functional theory calculations at the B3LYP/6-31G* level. Compound



Scheme 2. Acetylation of 5-azo-2-amino-thiazoles.

4A-a ($\mu = 3.08$ Db) has the azo tautomer 8.9 kcal mol^{-1} more stable than an alleged hydrazo form ($\mu = 6.71$ Db). This energetic difference decreases to 4.2 kcal mol^{-1} by variations in the calculated solvation energies for aqueous solutions. It is to be concluded that the azo tautomers **4** are not accompanied by substantial amounts of the hydrazo tautomers (not drawn). Therefore, the hypsochromic shift in the absorption spectra by the N-acetyl group (Tables 5 and 1) should be attributed to the decrease in the electron donating ability of the 2-amino function.

2.3. Reaction of 5-arylazothiazoles 2 with benzoyl chloride

The 2-amino-5-arylazothiazoles **2** were treated with benzoyl chloride in dry pyridine to give 2-benzamido-5-arylazothiazoles **5** as highly colored compounds (Scheme 3).

Table 5
Characterization data of the compounds **4A**

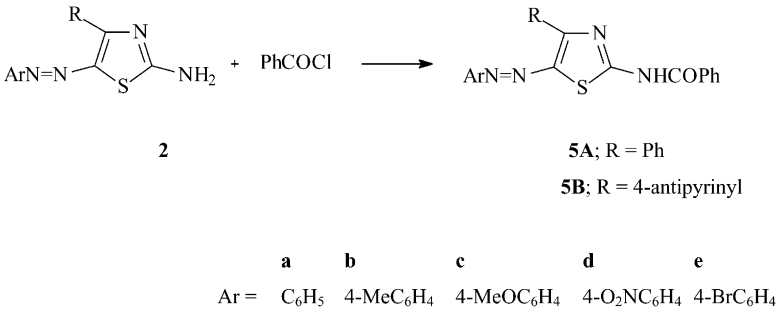
Cpd. no.	M.p. °C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula Mol. wt.	HRMS-C / HRMS-F
4A-a	211-212 (EtOH)	62 (orange)	408 (20,700)	3174, 3059, 2950, 1664, 1578, 1537, 1480, 1445, 1394, 1328, 1295, 1281.	$C_{17}H_{14}N_4OS$ 322	322.0888 322.0880
4A-b	219-220 (EtOH)	67 (red)	411 (19,750)	3165, 3043, 2953, 1661, 1602, 1533, 1482, 1443, 1383, 1328, 1294, 1280.	$C_{18}H_{16}N_4OS$ 336	336.1044 336.1041
4A-c	218–219 (EtOH)	78 (red)	417 (21,800)	3140, 3049, 2916, 1702, 1600, 1581, 1542, 1492, 1430, 1365, 1328, 1297.	$C_{18}H_{16}N_4O_2S$ 352	353.1072[a] 353.1073[a]
4A-d	>300 (DMF)	82 (violet)	439 (20,900)	3280, 1703, 1602, 1581, 1531, 1472, 1445, 1368, 1321, 1284, 1243, 1146.	$C_{17}H_{13}N_5O_3S$ 367	367.0739 367.0732
4A-e	261–262 (EtOH)	91 (red)	416 (21,400)	3174, 3037, 2928, 1646, 1570, 1546, 1473, 1444, 1411, 1377, 1326, 1286.	$C_{17}H_{13}BrN_4OS$ 401	401.0072 401.0068[a]

HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).
[a] M + H; chemical ionization (i-butane).

Table 6
Characterization data of the compounds **4B**

Cpd. no.	M.p. °C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula	HRMS-C / HRMS-F
4B-a	255 (EtOH)	71 (orange)	415 (19,300)	1696, 1631, 1591, 1548, 1496, 1425, 1365, 1339.	$C_{22}H_{20}N_6O_2S$	432.1368 / 432.1374
4B-b	292 (EtOH)	85 (orange)	417 (18,900)	1698, 1646, 1591, 1532, 1490, 1417, 1357, 1337.	$C_{23}H_{22}N_6O_2S$	446.1525 / 446.1524
4B-c	215 (EtOH)	77 (orange)	420 (20,500)	1696, 1658, 1598, 1544, 1491, 1415, 1349, 1291.	$C_{23}H_{22}N_6O_3S$	462.1474 / 462.149
4B-d	245 (DMF)	80 (red)	466 (20,000)	1704, 1647, 1590, 1519, 1411, 1369, 1323, 1217.	$C_{22}H_{19}N_7O_4S$	477.1219 / 477.1215
4B-e	270 (EtOH)	83 (orange)	424 (20,650)	1699, 1652, 1592, 1526, 1408, 1336, 1288, 1217.	$C_{22}H_{19}BrN_6O_2S$	512.0455 / 512.0432

HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).



Scheme 3. Benzoylation of 5-azo-2-amino-thiazoles.

Assignment of the products was based on their spectral data UV, IR, NMR and MS, which are given in Tables 7 and 8 (Experimental). The IR spectra of the 2-thiazolyl azo dye derivatives **5A** are characterized by the presence of strong absorption band of the carbonyl group (CO) at 1669–1682 cm^{-1} and a strong absorption band of NH group at 3400–3371 cm^{-1}. Moreover the high-resolution mass spectra are consistent with the calculated high-resolution mass spectra for the molecular formulas of the derivatives **5A** (Experimental) and **5B** (Table 8).

The azo tautomer structure for isolated molecules of **5** has been secured by density functional theory calculations at the B3LYP/6-31G* level. The azo-compound **5A-a** calculates more stable than its hydrazo tautomer by 3.9 kcal mol^{-1}. However, the dipole moment of **5A** (3.29 Db) is calculated lower than the one of the hydrazo tautomer (6.05 Db) and the energies of solvation (in water) decrease the energetic advantage of compound **5A-a** over its hydrazo tautomer (not drawn) to only 0.4 kcal mol^{-1}. Thus, an equilibrium of azo and hydrazo form is expected in

Table 7
Characterization data of the compounds **5A**

Cpd. no.	M.p. ° C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula Mol. wt.	HRMS-C / HRMS-F
5A-a	223 (A)	69 (red)	412 (20,600)	3400, 3059, 1671, 1601, 1580, 1533, 1478, 1455, 1394, 1328, 1283, 1246.	$C_{22}H_{16}N_4OS$ 384	384.1044 384.1045
5A-b	234 (A)	66 (red)	415 (21,000)	3399, 3061, 2917, 1672, 1600, 1580, 1532, 1481, 1455, 1386, 1325, 1283.	$C_{23}H_{18}N_4OS$ 398	398.1201 398.1192
5A-c	233 (A)	74 (red)	422 (21,450)	3399, 3052, 2936, 1672, 1601, 1580, 1534, 1500, 1481, 1329, 1290, 1250.	$C_{23}H_{18}N_4O_2S$	414.1151
5A-d	265 (A)	81 (red)	445 (23,500)	3371, 3061, 1682, 1602, 1583, 1526, 1445, 1420, 1372, 1322, 1255, 1193.	$C_{22}H_{15}N_5O_3S$ 429	429.0895 429.0896
5A-e	248 (A)	78 (red)	420 (21,200)	3397, 3060, 2929, 1669, 1600, 1580, 1533, 1469, 1412, 1381, 1326, 1285.	$C_{22}H_{15}BrN_4OS$ 463	462.0150 462.0158

(A) = EtOH + DMF. HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV).

Table 8
Characterization data of the compounds **5B**

Cpd. no.	M.p. °C (solvent)	Yield% (color)	UV: λ_{max} (ε) (MeOH)	IR Spectral data: cm^{-1}	Mol. formula	HRMS-C / HRMS-F
5B-a	251 (A)	71 (orange)	413 (21,750)	1671, 1639, 1591, 1537, 1495, 1420, 1294, 1254.	$C_{27}H_{22}N_6O_2S$	494.1525 494.1524
5B-b	246 (A)	85 (orange)	414 (22,650)	1668, 1636, 1591, 1538, 1495, 1410, 1290, 1242.	$C_{28}H_{24}N_6O_2S$	508.1681 508.1687
5B-c	244 (A)	77 (orange)	419 (21,600)	1668, 1635, 1596, 1539, 1497, 1417, 1294, 1248.	$C_{28}H_{24}N_6O_3S$	524.1630 524.1631
5B-d	262 (A)	80 (red)	465 (23,400)	1669, 1648, 1625, 1588, 1521, 1412, 1323, 1287.	$C_{27}H_{21}N_7O_4S$	539.1375 539.1380
5B-e	254 (A)	83 (orang)	423 (20,600)	1667, 1638, 1591, 1537, 1495, 1407, 1294, 1253.	$C_{27}H_{21}BrN_6O_2S$	572.0630 572.0632

HRMS: High Resolution Mass Spectrum; C = Calculated; F = Found (70 eV) (A): EtOH + DMF.

aqueous solution and one might predict that the crystal lattice contains the hydrazo forms of **5** for reasons of their higher polarity [9,11]. This energetic prediction should, of course, be verified by X-ray crystal structure determinations, as only the azo form **5A** is nearly planar. A first indication for the occurrence of the hydrazo form may be the strong hypsochromic effect if the benzoyl group is introduced (Table 7 and Table 1). However, even the equilibrating part of **5** should contribute to the hypsochromic shift due to the decreased ability of the aminobenzoyl group for providing electrons to the extended conjugated system.

2.4. Electronic absorption spectra

The electronic spectra of the dyes **2**–**5** were recorded in methanol. Color and absorption maxima are listed in Tables 1–8. There is an intense band at a λ_{max} ranging from 408–512 nm on the absorption spectra of 5-arylazothiazoles **2**–**5**. It was observed in general that

(a) the introduction of a methyl group into the coupling component of the dyes **2** causes bathochromic shifts in the dyes **3** of 5–20 nm;
(b) the introduction of acetyl or benzoyl groups into the coupling component of dyes **2** results in hypsochromic shifts in the dyes **4** and **5** of 12–52 nm;
(c) the bathochromic shift accompanying the substituents in the diazo component is in the following order; $H \rightarrow CH_3 \rightarrow OCH_3 \approx Br \rightarrow NO_2$;
(d) the bathochromic shift of the NO_2 groups is particularly large.

2.5. Dyeing of polyester fabrics and dyeing properties [13]

For some time an effort has been made to replace certain anthraquinone disperse dyes by azo dyes often derived from coupling of diazonium salts with heterocyclic compounds. Especially useful in this respect are dyes derived from derivatives of 2-aminothiazole and 2-pyridone as coupling components.

The 5-arylazo-thiazoles **2**–**5** were synthesized to assess their dyeing properties on polyester. The dyeing of polyester fabrics was performed at 2% shade by high-temperature techniques and gave generally deep and bright intense hues, ranging from yellow to red-violet.

2.5.1. Assessment of color fastness

Versatility is the first technical property of the present dyes to be emphasized. 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 following generalization can be drawn:

(a) Excellent behavior is shown in the fastnesses to washing at 50 °C and to perspiration.
(b) 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 these dye molecules into the fabrics.
(c) Sublimation fastness of the dyes is dependent upon the structure of the coupling component and was influenced by the substituents in the thiazole ring. Most of the dyes showed good sublimation fastness.
(d) The light fastness of 5-arylazo-thiazole dyes **2**–**5** on polyester is significantly affected by the nature of the substituents in the diazo component. In this study, the inclusion of the electron-withdrawing (nitro or bromo) groups improves the light fastness. In most cases, the best light fastness was obtained by the dyes containing a nitro group in the diazo component (e.g. dyes **4A-d**, **4B-d** and **5A-d**).

2.5.2. Color assessment

The color of the dyed fabrics was assessed by tristimulus colorimetry. The results are shown in Tables 10 and 12. It was observed that

(a) the color hues of the dyes **2**–**5** on polyester fabrics are shifted towards the reddish and

Table 9
Fastness properties of the dyes **2A**, **2B**, **3A** and **3B** on polyester fabrics

Dye no.	Washing	Perspiration		Rubbing		Sublimation fastness			Light (40 h)
		Acid	Alkali	Dry	Wet	Change in tone	Staining at 180 °C	Staining at 210 °C	
2A-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4
2A-b	4–5	4	4–5	4	4	4–5	4	4	3–4
2A-c	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	4
2A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4
2A-e	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4
2B-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	3–4
2B-b	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	2–3
2B-c	4–5	4–5	4–5	3–4	3–4	4–5	4–5	4–5	3–4
2B-d	4–5	4–5	4–5	3–4	4	4–5	4–5	4–5	5–6
2B-e	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4
3A-a	4–5	4–5	4–5	3–4	4	4	3–4	3	3
3A-b	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4	2–3
3A-c	4–5	4–5	4–5	4–5	4–5	4	3–4	3–4	4
3A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	3–4
3A-e	4–5	4–5	4–5	4	4–5	4–5	4	3–4	3
3B-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	3
3B-b	4–5	4–5	4–5	4	4	4–5	4–5	4–5	2–3
3B-c	4–5	4	4–5	3–4	4	4–5	4–5	4–5	2–3
3B-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4
3B-e	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	2–3

Table 10
Color of the dyes **2A**, **2B**, **3A** and **3B** on polyester fabrics

Dye no.	Color coordinates					CIELAB difference				K/S
	L^*	a^*	b^*	C^*	H	ΔL	ΔC	ΔH	ΔE	
2A-a	57.83	23.97	41.74	48.13	60.12	–	–	–	–	05.88
2A-b	62.25	37.87	73.69	82.85	62.80	04.42	34.72	02.95	35.12	17.81
2A-c	52.80	35.54	59.25	69.10	59.04	−05.02	20.96	−01.09	21.58	18.85
2A-d	32.17	42.03	19.64	46.39	25.05	−25.66	−01.74	−28.47	38.37	19.75
2A-e	58.16	46.03	68.95	82.90	56.27	00.32	34.77	−04.24	35.03	19.50
2B-a	72.00	19.38	25.90	32.35	53.19	–	–	–	–	01.23
2B-b	67.26	18.87	29.06	34.65	57.01	−04.73	02.30	02.22	05.72	01.80
2B-c	62.52	12.16	23.51	26.47	62.66	−09.48	−05.88	04.82	12.15	01.97
2B-d	74.18	08.68	23.83	25.36	69.99	02.18	−06.98	08.36	11.11	00.82
2B-e	74.74	12.19	27.31	29.90	65.94	02.74	−02.44	06.90	07.82	00.91
3A-a	62.29	38.47	74.79	84.10	62.78	–	–	–	–	18.77
3A-b	66.27	43.08	80.28	91.11	61.78	03.97	07.01	−01.52	08.20	17.73
3A-c	55.05	58.82	60.28	84.22	45.70	−07.24	−06.31	−08.53	12.85	21.03
3A-d	34.17	45.51	12.23	47.13	15.04	−28.12	−36.97	−50.94	68.94	17.12
3A-e	63.71	47.97	71.23	85.88	56.05	01.41	01.77	−09.98	10.23	15.40
3B-a	82.55	11.88	23.76	26.57	63.43	–	–	–	–	00.46
3B-b	75.07	19.65	37.38	42.23	62.27	−07.47	15.66	−00.68	17.36	01.31
3B-c	75.59	12.08	26.07	28.73	65.14	−06.96	02.16	00.82	07.33	00.83
3B-d	59.88	18.59	24.94	31.11	53.29	−22.66	04.53	−05.08	23.66	01.85
3B-e	71.60	24.18	48.47	54.16	63.49	−10.94	27.59	00.03	29.68	02.57

Table 11
Fastness properties of the dyes **4A**, **4B**, **5A** and **5B** on polyester fabrics

Dye no.	Washing	Perspiration		Rubbing		Sublimation fastness			Light (40 h)
		Acid	Alkali	Dry	Wet	Change in tone	Staining at 180 °C	Staining at 210 °C	
4A-a	4–5	4–5	4–5	4–5	4–5	4	4	3	7
4A-b	4–5	4–5	4–5	4	4–5	4–5	4	3–4	6–7
4A-c	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	6–7
4A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	7–8
4A-e	4–5	4–5	4–5	3–4	4	4–5	4–5	4	7
4B-a	4–5	4–5	4–5	4	4	4–5	4–5	4	4–5
4B-b	4–5	4	4–5	4	4–5	4–5	4–5	4–5	4–5
4B-c	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	5–6
4B-d	4–5	4–5	4–5	2–3	3	4–5	4–5	4–5	6–7
4B-e	4–5	4–5	4–5	3–4	4	4–5	4–5	4	6
5A-a	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	7
5A-b	4–5	4	4–5	4	4	4–5	4–5	4–5	7
5A-c	4–5	4–5	4–5	3	3–4	4–5	4–5	4–5	6–7
5A-d	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	6–7
5A-e	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	6–7
5B-a	4–5	4–5	4–5	3–4	3–4	4–5	4–5	4–5	6
5B-b	4–5	4–5	4–5	3–4	3	4–5	4–5	4	4–5
5B-c	4–5	4–5	4–5	4	3–4	4–5	4	4	4–5
5B-d	4–5	4–5	4–5	1–2	2	4–5	4–5	4–5	6
5B-e	4–5	4–5	4–5	3	3–4	4–5	4–5	4–5	4–5

Table 12
Color of the dyes **4A**, **4B**, **5A** and **5B** on polyester fabrics

Dye no.	Color coordinates					CIELAB difference				K/S
	L^*	a^*	b^*	C^*	H	ΔL	ΔC	ΔH	ΔE	
4A-a	59.39	35.98	71.35	79.91	63.24	–	–	–	–	20.65
4A-b	68.34	39.11	86.95	95.34	65.78	08.94	15.43	03.87	18.25	20.84
4A-c	67.50	40.77	86.98	96.06	64.89	08.11	16.15	02.52	18.25	21.84
4A-d	57.97	46.93	64.42	79.70	53.92	−01.42	−00.20	−12.96	13.04	16.55
4A-e	69.98	35.01	87.97	94.68	68.30	10.58	14.77	7.67	19.73	20.28
4B-a	77.83	13.09	57.09	58.57	77.09	–	–	–	–	03.15
4B-b	79.26	15.15	66.14	67.86	77.10	01.43	09.28	00.01	09.39	03.91
4B-c	69.83	13.79	40.45	42.73	71.17	−08.00	−15.84	−05.16	18.48	02.41
4B-d	67.66	27.43	19.33	33.55	35.17	−10.16	−25.01	−31.71	41.65	01.37
4B-e	75.35	25.77	56.61	62.20	65.52	−02.48	03.62	−12.16	12.93	03.18
5A-a	67.11	32.22	82.52	88.58	68.67	–	–	–	–	20.10
5A-b	74.14	27.18	91.91	95.85	73.53	07.03	07.26	07.80	12.77	19.84
5A-c	71.22	35.43	91.61	98.22	68.85	04.11	09.64	00.29	10.48	20.56
5A-d	54.80	50.56	63.08	80.84	51.29	−12.31	−07.74	−25.58	29.42	19.67
5A-e	69.84	37.91	87.11	95.00	66.38	02.73	06.42	−03.51	07.81	18.77
5B-a	75.78	25.41	69.52	74.01	69.92	–	–	–	–	05.25
5B-b	79.62	18.87	58.75	61.70	72.19	03.84	−12.31	02.67	13.17	02.59
5B-c	72.16	30.33	70.69	76.92	66.77	−03.62	02.90	−04.14	06.22	07.21
5B-d	61.27	32.63	13.05	35.14	21.79	−14.50	−38.87	−41.59	58.74	01.91
5B-e	75.22	27.67	53.36	60.11	62.59	−00.55	−13.90	−08.52	16.32	02.82

yellowish directions on the red-green and yellow-blue axes, respectively;

(b) the 2-amino-4-antipyrinyl-thiazole dyes **2B–5B** are more light than the corresponding 4-phenyl-thiazole dyes **2A–5A** according to the color lightness values (L*);

(c) the 2-amino-4-phenyl-thiazole dyes **2A–5A** are brighter than the corresponding 2-amino-4-antipyrinyl-thiazole dyes **2B–5B** according to the color brightness values (C*).

3. Conclusions

A set of 40 disperse dyes **2–5**, from which only **2A-a–2A-d** were previously described [10], were synthesized by azo coupling and modification by acetylation and benzoylation. All of them were investigated for their dyeing characteristics on polyester. The electronic absorption spectra cover a λ_{max} range of 408–512 nm at uniformly high absorption intensity and give bright intense hues from yellow to red-violet on polyester fabrics, due to the variations in polarity. The changes in color coordinates between the A- and B-series (Tables 10 and 12) is remarkable in view of minor variations of the absorption maxima in solution. The dyed fabrics exhibit very good to excellent (4–5) washing, perspiration and sublimation fastness properties (Tables 9 and 11) with little variations in the good to excellent rubbing fastness. Only the benzoylated dyes **5A-c** and **5B-a–e** as well as the acetylated dye **4B-d** exhibit some decrease in the latter property. The remarkable degree of levelness and 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. This in combination with the ease of preparation makes them particularly valuable.

4. Experimental

All melting points were uncorrected. IR spectra (KBr) were recorded with a Perkin-Elmer 1720-X FT-IR spectrometer (not all frequencies are reported). 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 for water are calculated on the basis of the B3LYP results using the semiempiric SM5.4/A routine.

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

Preparation of the diazonium salt: A solution of sodium nitrite (0.7 g in 10 ml water) was gradually added to a well cooled (0 °C) solution of the aromatic amine (0.01 mol) in conc. HCl (3.0 ml). The diazonium salt solution was added with continuous stirring to a cold (0 °C) solution of the 2-amino-thiazole derivative **1** in ethanol (50 ml) and sodium acetate (4 g). The reaction mixture was allowed to stand in the cold for 2 h and then filtered. The 2-amino-5-arylazothiazoles thus obtained, were dried and recrystallized from the appropriate solvent.

2B-a, ^{1}H-NMR (DMSO): δ/ppm = 2.40 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.20–7.40 (m, 6 Ar-H), 7.50 (ψd, 2 Ar-H), 7.60 (ψd, 2 Ar-H), 8.05 (s, 2H, NH_2); ^{13}C-NMR (DMSO): δ/ppm = 10.78, 33.46, 102.00, 119.69 (2C), 122.92 (2C), 124.94, 126.51, 127.15 (2C), 127.23 (2C), 133.38, 137.62, 148.62, 150.97, 153.18, 161.08, 168.25; MS (EI): m/z (%) = 390 (M, 100), 298, 269, 242, 186, 124, 93, 56.

2B-b, ^{1}H-NMR ($CDCl_3$): δ/ppm = 2.35 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 7.15 (ψd, 2 Ar-H), 7.25–7.60 (m, 9 Ar-H and NH_2); ^{13}C-NMR ($CDCl_3$): δ/ppm = 13.09, 21.33, 35.20, 104.45, 121.79 (2C), 125.52 (2C), 127.42, 129.28 (2C), 129.56 (2C), 134.73, 139.09, 140.97, 147.34, 150.93, 154.38, 163.31, 170.31; MS (EI): m/z (%) = 404 (M, 100), 312, 283, 256, 214, 106, 91, 56.

2B-c, ^{1}H-NMR ($CDCl_3$): δ/ppm = 2.30 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.85 (ψd, 2 Ar-H), 7.25–7.50 (m, 7 Ar-H and NH_2), 7.60 (ψd, 2 Ar-H); ^{13}C-NMR ($CDCl_3$): δ/ppm = 13.03, 35.20, 55.44, 104.35, 114.12 (2C), 123.37 (2C), 125.47 (2C), 127.36, 129.25 (2C), 134.73, 141.10, 146.39, 147.22, 154.30, 160.36,

163.35, 169.98; MS (EI): *m/z* (%) = 420 (M), 392, 329, 299 (100), 286, 229, 204, 189, 140, 123, 108, 77, 56.

2B-d, ^{1}H-NMR (CF_3COOD): δ/ppm = 2.80 (s, 3H, CH_3), 3.60 (s, 3H, CH_3), 7.45 (ψd, 2 Ar-H), 7.60–7.85 (m, 5 Ar-H), 8.35 (ψd, 2 Ar-H); ^{13}C-NMR (CF_3COOD): δ/ppm = 13.28, 33.89, 96.16, 122.43, 125.61 (2C), 128.71 (2C), 129.71(2C), 131.10, 132.93 (2C), 137.22, 141.96, 148.31, 149.56, 153.05, 160.10, 171.68.

2B-e, ^{1}H-NMR (DMSO): δ/ppm = 2.40 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.30-7.65 (m, 9 Ar-H), 8.35 (s, 2H, NH_2); ^{13}C-NMR (DMSO): δ/ppm = 12.32, 35.05, 102.86, 120.84, 123.16 (2C), 124.83 (2C), 126.86, 129.13 (2C), 132.06 (2C), 135.10, 138.57, 151.78, 152.20, 154.90, 162.63, 170.17; MS (EI): *m/z* (%) = 470 (^{81}Br, M), 468 (^{79}Br, M), 378, 376, 322, 320, 286, 171, 56 (100).

3A-a, ^{1}H-NMR ($CDCl_3$–DMSO): δ/ppm = 3.00 (s, 3H, CH_3), 7.20–7.40 (m, 6 Ar-H), 7.60 (ψd, 2 Ar-H), 8.20 (ψd, 2 Ar-H), 8.50 (sb, 1 NH); ^{13}C-NMR ($CDCl_3$/DMSO): δ/ppm = 29.97 (CH_3), 120.63 (2 Ar-C), 127.03 (2 Ar-C), 127.41(1 Ar-C), 127.89 (2 Ar-C), 128.36 (Ar-C), 129.14 (2 Ar-C), 132.66 (Ar-C), 138.58 (thiazole C-5), 151.19 (Ar-C), 154.56 (thiazole C-4), 169.30 (thiazole C-2).

3A-b, ^{1}H-NMR ($CDCl_3$-CF_3COOD): δ/ppm = 2.40 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.30 (ψd, 2 Ar-H), 7.50-7.70 (m, 5Ar-H), 7.95 (d, 2 Ar-H).

3A-c, ^{1}H-NMR ($CDCl_3$-CF_3COOD): δ/ppm = 3.25 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 7.15 (ψd, 2 Ar-H), 7.65–7.75 (m, 3 Ar-H), 7.95 (ψd, 2 Ar-H), 8.05 (ψd, 2 Ar-H). MS (EI): *m/z* (%) = 324 (M, 100), 309, 190, 162, 133, 107, 77.

3A-d, MS (EI): *m/z* (%) = 339 (M, 100), 292, 189, 145, 133, 104, 89, 74.

3A-e, HRMS (EI): $C_{16}H_{13}$ $^{79}BrN_4S$ calcd.: 372.0044 found: 372.0052

3B-a, ^{1}H NMR (CF_3COOD): δ/ppm = 2.70 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.60 (s, 3H, CH_3), 7.35–7.70 (m, 10 Ar-H). MS (EI): *m/z* (%) = 404 (M, 100), 312, 284, 256, 243, 226, 93, 77, 56.

3B-b, ^{1}H-NMR (DMSO): δ/ppm = 2.35 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.20 (ψd, 2 Ar-H), 7.30–7.60 (m, 7 Ar-H), 8.20 (s, 1 NH); ^{13}C-NMR (DMSO): δ/ppm = 11.66, 20.14, 29.96, 34.26, 103.46, 120.49 (2C), 123.69 (2C), 125.78, 127.99 (2C), 128.47 (2C), 133.99, 137.45, 138.76, 148.00, 149.79, 153.85, 162.05, 169.38. MS (EI): *m/z* (%) = 418 (M, 100), 366, 326, 298, 270, 243, 214, 131, 91, 56.

3B-c, ^{1}H-NMR (CF_3COOD): δ/ppm = 2.70 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 7.00 (ψd, 2 Ar-H), 7.40 (ψd, 2 Ar-H), 7.60–7.80 (m, 5 Ar-H); ^{13}C-NMR (CF_3COOD): δ/ppm = 12.77, 33.32, 33.71, 55.84, 95.38, 115.19 (2C), 125.17, 128.28, 128.52 (2C), 129.10, 129.72, 130.79 (2C), 132.49 (2C), 137.60, 148.60, 159.06, 163.30, 169.67. MS (EI): *m/z* (%) = 434 (M, 100), 419, 342, 314, 286, 243, 214, 207, 135, 107, 77, 56.

3B-d, ^{1}H-NMR (CF_3COOD): δ/ppm = 2.80 (s, 3H, CH_3), 3.40 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 7.45 (ψd, 2 Ar-H), 7.70–7.85 (m, 5 Ar-H), 8.30 (ψd, 2 Ar-H); MS (EI): *m/z* (%) = 449 ((M, 100), 419, 357, 328, 301, 195, 165, 77, 56.

3B-e, ^{1}H-NMR (DMSO): δ/ppm = 2.40 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.40-7.80 (m, 9H, Ar-H), 8.90 (s, 1 NH); ^{13}C-NMR (DMSO): δ/ppm = 12.26, 30.63, 35.00, 102.88, 120.78, 123.13 (2C), 124.85 (2C), 126.86, 129.11 (2C), 132.04 (2C), 133.69, 135.06, 138.28, 151.75, 152.06, 154.94, 162.59. MS (EI): *m/z* (%) = 484 (^{81}Br, M, 100), 482 (^{79}Br, M), 392, 390, 336, 334, 312, 243, 93, 77, 56.

4.2. Synthesis of 2-acetylamino-5-arylazothiazoles (4)

A mixture of the 2-amino-5-arylazothiazole **2** (3.0 mmol) and acetic anhydride (3.0 ml) was heated in an oil bath at 60–65 °C for 1 h. The reaction mixture was allowed to cool at room temperature and then recrystallized from the appropriate solvent.

4A-a, ^{1}H-NMR ($CDCl_3$): δ/ppm = 1.75 (s, 3H, CH_3), 7.40–7.55 (m, 6 Ar-H), 7.85 (ψd, 2 Ar-H), 8.20 (ψd, 2 Ar-H), 11.40 (s, 1 NH); ^{13}C-NMR ($CDCl_3$): δ/ppm = 22.63, 122.97 (2C), 128.71 (2C), 129.14 (2C), 129.56, 130.05 (2C), 130.66, 133.57, 144.96, 150.15, 152.50, 160.47, 168.67. MS (EI): *m/z* (%) = 322 (M), 279 (100), 174, 133, 104, 89, 77.

4A-b, ^{1}H-NMR ($CDCl_3$): δ/ppm = 1.75 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 7.25 (ψd, 2 Ar-H), 7.40-7.55 (m, 3 Ar-H), 7.75 (ψd, 2 Ar-H), 8.20 (ψd, 2

Ar-H), 11.35 (s, 1 NH); ^{13}C-NMR ($CDCl_3$): δ/ppm = 21.51, 22.69, 122.96 (2C), 128.67 (2C), 129.43, 129.82 (2C), 129.97 (2C), 133.55, 141.35, 145.07, 149.17, 150.63, 160.07, 168.58.

4A-c, ^{1}H-NMR (DMSO): δ/ppm = 2.25 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 7.00 (ψd, 2 Ar-H), 7.35–7.50 (m, 3 Ar-H), 7.75 (ψd, 2 Ar-H), 8.20 (ψd, 2 Ar-H), 12.05 (s, 1 NH); ^{13}C-NMR (DMSO): δ/ppm = 22.46, 54.99, 113.86 (2C), 123.86 (2C), 127.70 (2C), 128.29, 129.23 (2C), 133.63, 144.20, 146.30, 148.74, 158.09, 160.96, 168.74. MS (EI): m/z (%) = 352 (M, 100), 309, 295, 174, 148, 133, 121, 107, 77.

4A-d, see Table 5.

4A-e, MS (EI): m/z (%) = 402 (^{81}Br, M), 400 (^{79}Br, M), 359 (100), 357, 198, 196, 157, 159, 133, 104, 76.

4B-a, ^{1}H-NMR ($CDCl_3$): δ/ppm = 2.20 (s, 3 acetyl-H), 2.35 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.30–07.50 (m, 8 Ar-H), 7.75 (ψd, 2 Ar-H), 11.60 (s, 1 NH); ^{13}C-NMR ($CDCl_3$): δ/ppm = 12.04, 22.35, 34.58, 103.30, 121.59 (2C), 124.64 (2C), 126.72, 128.45 (2C), 128.60 (2C), 129.47, 134.14, 144.06, 144.88, 151.90, 153.65, 159.21, 162.59, 168.72; MS (EI): m/z (%) = 432 (M), 390, 339, 297, 282, 243, 165, 135, 105, 93, 77, 56 (100).

4B-b, ^{1}H-NMR ($CDCl_3$): δ/ppm = 2.00 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.20 (ψd, 2 Ar-H), 7.25–7.45 (m, 5 Ar-H), 7.65 (ψd, 2 Ar-H), 11.40 (s, 1 NH); ^{13}C-NMR ($CDCl_3$): δ/ppm = 12.60, 21.43, 22.98, 35.21, 104.62, 122.33 (2C), 125.42 (2C), 127.49, 129.28 (2C), 129.69 (2C), 134.51, 140.64, 144.15, 145.50, 150.78, 154.14, 159.53, 163.72, 169.19; MS (EI): m/z (%) = 446 (M), 404, 376, 339, 328 (100), 298, 286, 236, 197, 106, 77.

4B-c, ^{1}H-NMR ($CDCl_3$): δ/ppm = 2.00 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.95 (ψd, 2 Ar-H), 7.25–7.50 (m, 5 Ar-H), 7.75 (ψd, 2 Ar-H), 11.50 (s, 1 NH); ^{13}C-NMR ($CDCl_3$): δ/ppm = 12.63, 23.08, 35.30, 55.59, 104.64, 114.32 (2C), 124.21 (2C), 125.40 (2C), 127.49, 129.31 (2C), 134.57, 143.12, 145.60, 147.10, 154.21, 159.12, 161.53, 163.71, 169.26. MS (EI): m/z (%) = 462 (M), 420, 392, 339, 328, 298, 286, 214, 135, 77, 56 (100).

4B-d, ^{1}H-NMR (CF_3COOD): δ/ppm = 2.40 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 7.45–7.65 (m, 5 Ar-H), 7.85 (ψd, 2 Ar-H), 8.30 (ψd, 2 Ar-H); ^{13}C-NMR (CF_3COOD): δ/ppm = 12.99, 22.58, 33.75, 98.05, 123.73 (2C), 125.66 (2C), 128.64 (2C), 129.32, 131.22 (2C), 133.31, 141.39, 143.59, 149.11, 149.47, 154.72, 157.64, 162.27, 173.00. MS (EI): m/z (%) = 477 (M), 435, 339 (100), 298, 286, 268, 240, 213, 138, 108, 77.

4B-e, ^{1}H-NMR ($CDCl_3$-CF_3COOD): δ/ppm = 2.20 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 7.40-7.60 (m, 9 Ar-H); ^{13}C-NMR (DMSO): δ/ppm = 10.51, 21.02, 33.28, 101.10, 121.40, 121.95 (2C), 123.08 (2C), 125.06, 127.23 (2C), 130.36 (2C), 133.21, 141.40, 145.18, 149.49, 152.79, 157.93, 160.93, 167.40: MS (EI): m/z (%) = 512 (^{81}Br, M), 510 (^{79}Br, M), 470, 468, 380, 353, 339, 297 (100), 282, 253, 224, 194, 171, 135.

4.3. Synthesis of 2-benzoylamino-5-arylazothiazoles (5)

A mixture of the 2-amino-5-arylazothiazole **2** (3.0 mmol) and benzoyl chloride (0.35 ml, 3.0 mmol) was stirred in 15 ml pyridine at room temperature. The reaction mixture was diluted by a solution of sodium acetate and filtered. The 2-benzoylamino-5-arylazothiazoles thus obtained were dried and recrystallized from the proper solvent.

5A-a, ^{1}H-NMR (CF_3COOD): δ/ppm = 7.45–7.95 (m, 13 Ar-H), 8.05 (ψd, 2 Ar-H).

5A-b, ^{1}H-NMR (CF_3COOD): δ/ppm = 2.40 (s, 3H, CH_3), 7.30 (ψd, 2 Ar-H), 7.55-7.90 (m, 10 Ar-H), 8.05 (ψd, 2 Ar-H).

5A-c, ^{1}H-NMR (CF_3COOD): δ/ppm = 3.90 (s, 3H, CH_3), 7.05 (ψd, 2 Ar-H), 7.55-7.95 (m, 10 Ar-H), 8.05 (ψd, 2 Ar-H); ^{13}C-NMR (CF_3COOD): δ/ppm = 55.93, 115.13 (2C), 126.26 (2C), 126.48, 128.63 (2C), 129.32 (3C), 129.56 (4C), 131.85, 135.35, 138.16, 142.99, 146.07, 162.65, 163.74, 167.02.

5A-d, MS (EI): m/z (%) = 429 (M, 100), 324, 278, 174, 122, 105, 77.

5A-e, see Table 7.

5B-a, ^{1}H-NMR (DMSO): δ/ppm = 2.40 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.30–7.60 (m, 12 Ar-H and 1 NH), 7.75 (ψd, 2 Ar-H), 8.15 (ψd, 2 Ar-H); ^{13}C-NMR (DMSO): δ/ppm = 12.21, 35.05, 102.14, 122.03 (2C), 124.87 (2C), 126.93, 128.39 (2C), 128.55 (2C), 129.13 (2C), 129.35 (2C), 130.31,

131.83, 132.88, 133.61, 143.41, 146.07, 152.17, 154.83, 159.99, 162.77, 166.05; MS (EI): m/z (%) = 494 (M), 466, 401, 390, 313, 243, 105 (100), 77.

5B-b, ^{1}H-NMR (DMSO): δ/ppm = 2.35 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 7.25–7.50 (m, 11 Ar-H and 1 NH), 7.65 (ψd, 2 Ar-H), 8.00 (ψd, 2 Ar-H); ^{13}C-NMR ($CDCl_3$/CF_3-COOD): δ/ppm = 13.00, 21.61, 33.62, 97.15, 123.39 (2C), 128.13 (2C), 128.42 (2C), 129.40 (2C), 129.58, 129.70, 130.57 (2C), 130.78 (2C), 132.44, 134.80, 135.50, 142.38, 144.87, 148.75, 148.97, 158.28, 160.91, 166.02; MS (EI): m/z (%) = 508 (M), 480, 401, 390, 313, 243, 105 (100), 77.

5B-c, ^{1}H-NMR (DMSO): δ/ppm = 2.40 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.95 (ψd, 2 Ar-H), 7.35-7.80 (m, 11 Ar-H and 1 NH), 8.15 (ψd, 2 Ar-H); ^{13}C-NMR ($CDCl_3$/CF_3-COOD): δ/ppm = 12.87, 33.57, 55.82, 97.19, 115.25 (2C), 125.88 (2C), 128.09 (2C), 128.42 (2C), 129.36 (2C), 129.60, 130.73 (2C), 130.90, 132.36, 134.23, 134.72, 142.52, 145.06, 148.57, 158.18, 160.37, 164.03, 166.07; MS (EI): m/z (%) = 524 (M), 496, 401, 390, 313, 243, 105 (100), 77.

5B-d, ^{1}H-NMR (DMSO): δ/ppm = 2.50 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 7.35–7.60 (m, 9 Ar-H and 1 NH), 7.95 (ψd, 2 Ar-H), 8.15 (ψd, 2 Ar-H), 8.30 (ψd, 2 Ar-H); MS (EI): m/z (%) = 539 (M), 401 (100), 138, 105, 77.

5B-e, ^{1}H-NMR (DMSO): δ/ppm = 2.40 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.30-7.70 (m, 13 Ar-H and 1 NH), 8.10 (ψd, 2 Ar-H); MS (EI): m/z (%) = 474 (^{81}Br, M), 472 (^{79}Br, M^+), 546, 544, 401, 390, 327, 240, 171, 105 (100).

4.4. Dyeing and fastness determinations

4.4.1. Dyeing procedure

The fabric was dyed with 2.0% dye (calculated by weight of the fabric) and 1% Avolan IS (Bayer AG, Germany) as 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% of the dispersing agent Avolan IS at 70 °C for 30 min. Finally, the fabric was rinsed and dried at 60 °C.

4.4.2. Color fastness tests

The results are collected in the Tables 9 and 11.

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

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

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

(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 rest of the procedure was the same as in the dry test. The staining on the white testing cloth was assessed according to the grey scale: 1—poor, 2—fair, 3—moderate, 4—good, 5—excellent.

(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 °C and 210 °C each for 1 min. Any staining on the undyed adjacent fabric or change in tone was assessed

according to the following grey scale: 1—poor, 2—fair, 3—moderate, 4—good, 5—excellent.

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

4.4.3. Color assessment

Tables 10 and 12 report the color parameters of the dyed fabrics assessed by tristimulus colorimetry. The color parameters of the dyed fabrics were determined on a spectro multichannel photo detector (model MCPD-110A), equipped with a D65 source and barium sulphate as a standared blank. The color of dyed fabrics 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.

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