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New synthetic strategy for novel 6-arylazo-5-methyl-3-aryl-thiazolo[2,3-*c*]-[1,2,4]triazoles and study of their solvatochromic properties

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Abstract: Two series of 6-arylazothiazol[2,3-*c*][1,2,4]triazoles were prepared via oxidative cyclization of the respective aldehyde N-(5-arylazo-4-methylthiazol-2-yl)-hydrazones. The structures of the latter hydrazone precursors and the azo compounds were confirmed by spectral and elemental analyses. The solvatochromism of the title azo dyes is evaluated by means of the Kamlet–Taft equation and discussed.

Key words: Arylazoheterocycles, thiazole, 1,5-electrocyclization, solvatochromism, hydrazonoyl halides

1. Introduction

Many arylazo derivatives of heterocyclic compounds have found various applications in industry including hair dyeing, disperse dyes, ink-jet inks, and laser materials.[1,2] In the light of this and in continuation of our studies on exploring the utility of hydrazonoyl halides in the synthesis of aryl- and hetaryl-azo derivatives of heterocyclic compounds,[3–10] we wish to report herein a new synthetic strategy for the thiazolo[2,3-*c*][1,2,4]triazole ring system and its 6-arylazo derivatives, which have not been reported hitherto (Scheme 1). In addition, it was thought interesting to study the solvatochromic properties of such dyes via application of Kamlet–Taft equations[11,12] prior to exploring their applications.

2. Experimental

All melting points were determined on a Gallenkamp apparatus and are uncorrected. Solvents were generally distilled and dried by standard literature procedures prior to use. The IR spectra were measured on a Pye-Unicam SP300 instrument in potassium bromide disks. The ^{1}H NMR spectra were recorded on a Varian Mercury VXR-300 MHz spectrometer and the chemical shifts δ downfield from tetramethylsilane (TMS) as an internal standard. The mass spectra were recorded on GCMS-Q1000-EX Shimadzu and GCMS 5988-A HP spectrometers; the ionizing voltage was 70 eV. Elemental analyses were carried out by the Microanalytical Center of Cairo University, Giza, Egypt. Both the hydrazonoyl chlorides **1**[13] and substituted benzaldehyde thiosemicarbazones **2** were prepared as previously described.[14]

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2.1. Synthesis of substituted-benzaldehyde N-(5-arylazo-4-methylthiazol-2-yl)-hydrazones (3)

General procedure: To a mixture of benzaldehyde thiosemicarbazaone **2c** (0.01 mol) and the appropriate N-aryl-2-oxopropanehydrazonoyl chloride **1** (0.01 mol) in absolute ethanol (50 mL) was added triethylamine (1.01 g, 0.01 mol). The reaction mixture was refluxed for 5 h and then cooled to room temperature. The precipitate formed was filtered off, washed with water and ethanol, and finally crystallized from the appropriate solvent to give the corresponding benzaldehyde N-(5-arylazo-4-methyl-thiazol-2-yl)hydrazones **3A**.

When the above procedure was repeated using **2a–e** each with the hydrazonoyl halide **1c**, it yielded the respective substituted-benzaldehyde N-(5-phenylazo-4-methyl-thiazol-2-yl)hydrazones **3B**.

The compounds **3Aa–e** and **3Ba–e** prepared, together with their physical constants, are given below.

Benzaldehyde N-(5-methoxyphenylazo-4-methylthiazol-2-yl)-hydrazone (3Aa): brown solid, yield 2.24 g (64%), mp 215 °C; IR (KBr) ν 3171 (NH), 1240 (CH_3O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.65 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.92 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 7.45–7.50 (m, 5H, Ar-H), 7.85 (s, 1H, N=CH), 8.60 (s, 1H, NH); MS m/z (%) 352 (M^++1, 8), 351 (M^+, 34), 247 (5), 216 (6), 178 (4), 163 (2), 134 (13), 122 (72), 107 (35), 92 (24), 89 (41), 77 (100). Anal. Calcd. for $C_{18}H_{17}N_5OS$ (Mw 351.43): C, 61.52; H, 4.88; N, 19.93. Found: C, 61.66; H, 4.45; N, 20.20%.

Benzaldehyde N-(5-p-methylphenylazo-4-methylthiazol-2-yl)-hydrazone **(3Ab)**: reddish solid, yield 2.0 g (60%), mp 220–221 °C; IR (KBr) ν 3180 (NH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.35 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 7.12 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 7.45–7.50 (m, 5H, ArH), 7.90 (s, 1H, N=CH), 8.63 (s, 1H, NH); MS m/z (%) 336 (M^++1, 8), 335 (M^+, 50), 231 (15), 216 (6), 203 (3), 161 (6), 128 (8), 106 (38), 91 (92), 77 (100). Anal. Calcd. for $C_{18}H_{17}N_5S$ (Mw 335.43): C, 64.45; H, 5.11; N, 20.88. Found: C, 64.36; H, 5.26; N, 20.67%.

Benzaldehyde N-(5-phenylazo-4-methylthiazol-2-yl)-hydrazone (3Ac): brown solid, yield 2.0 g (62%), mp 195 °C; IR (KBr) ν 3190 (NH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.63 (s, 3H, CH_3), 7.0–7.4 (m, 5H, ArH), 7.90 (s, 1H, N=CH), 8.63 (s, 1H, NH); MS m/z (%) 322 (M^++1, 13), 321 (M^+, 89), 288 (5), 217 (30), 170 (7), 148 (13), 118 (7), 103 (19), 90 (40), 77 (100). Anal. Calcd. for $C_{17}H_{15}N_5S$ (Mw 321.41): C, 63.53; H, 4.70; N, 21.79. Found: C, 63.29; H, 5.02; N, 21.56%.

Benzaldehyde N-(5-p-chlorophenylazo-4-methylthiazol-2-yl)-hydrazone (3Ad): red solid, yield 2.2 g (64%), mp 218 °C; IR (KBr) ν 3177 (NH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.70 (s, 3H, CH_3), 7.45–7.50 (m, 5H, ArH), 7.82 (d, 2H, Ar-H), 7.89 (d, 2H, Ar-H), 7.90 (s, 1H, N=CH), 8.63 (s, 1H, NH); MS m/z (%) 356 (M^++1, 2.3), 355 (M^+, 1), 237 (1.2), 216 (2), 128 (4), 126 (15), 111 (37), 104 (7), 100 (4), 99 (13), 89 (28), 77 (18), 63 (23), 50 (100); Anal. Calcd. for $C_{17}H_{14}ClN_5S$ (Mw 355.85): C, 57.38; H, 3.97; N, 19.68. Found: C, 56.98; H, 3.81; N, 19.49%.

Benzaldehyde N-(5-p-nitrophenylazo-4-methylthiazol-2-yl)-hydrazone (3Ae): brown solid, yield 2.6 g (71%), mp 230–232 °C; IR (KBr) ν 3200 (NH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.70 (s, 3H, CH_3), 7.4–7.5 (m, 5H, ArH), 7.89 (d, 2H, Ar-H), 8.26 (d, 2H, Ar-H), 8.3 (s, 1H, N=CH), 8.70 (s, 1H, NH); MS m/z (%) 366 (M^+, 3), 216 (6), 183 (5), 172 (4), 161 (4), 134 (4), 122 (12), 117 (14), 103 (18), 89 (77), 76 (100); Anal. Calcd. for $C_{17}H_{14}N_6O_2S$ (Mw 366.40): C, 55.73; H, 3.85; N, 22.94. Found: C, 55.48; H, 3.74; N, 22.78%.

p-Methoxybenzaldehyde N-(5-phenylazo-4-methylthiazol-2-yl)-hydrazone (3Ba): brown solid, yield 2.8 g (80%), mp 170–173 °C; IR (KBr) ν 3273 (NH), 1240 (CH_3O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.67 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.80 (d, 2H, Ar-H), 7.5 (d, 2H, Ar-H), 7.35–7.50 (m, 5H, Ar-H), 7.80 (s, 1H,

N=CH), 8.60 (s, 1H, NH); MS m/z (%) 352 (M^+, 100), 323 (20), 245 (17), 216 (45), 211 (10), 147 (18), 134 (14), 119 (15), 104 (12), 91 (35), 77 (41). Anal. Calcd. for $C_{18}H_{17}N_5OS$ (351.43): C, 61.52; H, 4.88; N, 19.93. Found: C, 61.40; H, 4.90; N, 20.00%.

p-Methylbenzaldehyde N-(5-phenlazo-4-methylthiazol-2-yl)-hydrazone (3Bb): orange solid, yield 2.84 g (85%), mp 180–182 °C; IR (KBr) ν 3397 (NH) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 7.2 (d, 2H, Ar-H), 7.3 (d, 2H, Ar-H), 7.40–7.50 (m, 5H, ArH), 7.8 (s, 1H, N=CH), 8.6 (s, 1H, NH); MS m/z (%) 336 (M^++1, 3), 335 (M^+, 70), 302 (8), 244 (4), 217 (17), 197 (8), 148 (8), 118 (19), 103 (26), 91 (73), 77 (100). Anal. Calcd. for $C_{18}H_{17}N_5S$ (Mw 335.43): C, 64.45; H, 5.11; N, 20.88. Found: C, 64.18; H, 4.94; N, 20.33%.

p-Chlorobenzaldehyde N-(5-p-chlorophenylazo-4-methylthiazol-2-yl)-hydrazone (3Bd): orange solid, yield 2.9 g (81%), mp 205–207 °C; IR (KBr) ν 3417 (NH) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.7 (s, 3H, CH_3), 7.20 (d, 2H, Ar-H), 7.38 (d, 2H, Ar-H), 7.34–7.50 (m, 5H, ArH), 7.90 (s, 1H, N=CH), 8.63 (s, 1H, NH); MS m/z (%) 358 (M^++2, 3), 357 (M^++1, 46), 355 (M^+, 100), 244 (6), 217 (41), 170 (6), 137 (14), 111 (24), 92 (29), 77 (92); Anal. Calcd. for $C_{17}H_{14}ClN_5S$ (Mw 355.85): C, 57.38; H, 3.97; N, 19.68. Found: C, 56.98; H, 3.71; N, 19.86%.

p-Nitrobenzaldehyde N-(5-phenylazo-4-methylthiazol-2-yl)-hydrazone (3Be): reddish brown solid, yield 3.1 g (86%), mp 215–217 °C; IR (KBr) ν 3279 (NH) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.70 (s, 3H, CH_3), 7.3–7.4 (m, 5H, ArH), 7.5 (s, 1H, N=CH), 8.1 (d, 2H, Ar-H), 8.4 (d, 2H, Ar-H), 8.70 (s, 1H, NH); MS m/z (%) 367 (M^++1, 13), 366 (M^+, 100), 217 (13), 170 (4), 149 (20), 118 (8), 104 (6), 92 (26), 89 (6), 77 (78); Anal. Calcd. for $C_{17}H_{14}N_6O_2S$ (Mw 366.40): C, 55.73; H, 3.85; N, 22.94. Found: C, 55.52; H, 3.97; N, 22.58%.

2.2. Synthesis of 3-aryl-5-methyl-6-phenylazo[thiazolo[2,3-c][1,2,4]-triazoles (4)

General procedure: To a solution of the appropriate hydrazone **3** (2.5 mmol) in ethanol (50 mL) was added a solution of ferric chloride (2 M, 2 mL) and the mixture was refluxed for 45 min and then cooled to room temperature. The precipitated solid was filtered off, washed with water and then with ethanol, and finally crystallized from a chloroform–ethanol mixture to give the respective 3-phenyl-5-methyl-6-arylazo[thiazolo[2,3-c][1,2,4]-triazole **4** as a dark colored solid. The compounds **4A(B)a–e** prepared, together with their physical constants, are given below.

3-Phenyl-5-methyl-6-(p-methoxyphenylazo)-thiazolo[2,3-c][1,2,4]-triazole (4Aa): yield 0.54 g (62%), mp 200 °C; IR (KBr) ν 1243 (CH_3OC) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.7 (s, 3H, CH_3), 3.90 (s, 3H, $ArOCH_3$), 7.2 (d, 2H, Ar-H), 7.22–7.50 (m, 5H, Ar-H), 8.9 (d, 2H, Ar-H); MS m/z (%) 349 (M^+, 0.4), 227 (0.4), 216 (0.6), 196 (0.8), 171 (0.7), 150 (1.36), 139 (3), 122 (7), 91 (9), 89 (15), 76 (36), 50 (100). Anal. Calcd. for $C_{18}H_{15}N_5OS$ (Mw 349.42): C, 61.87; H, 4.33; N, 20.04. Found: C, 54.40; H, 4.53; N, 20.07%.

3-Phenyl-5-methyl-6-(p-methylphenylazo)-thiazolo[2,3-c][1,2,4]-triazole (4Ab): yield 0.47 g (56% yield), mp 205 °C; ^1H NMR (DMSO-d_6) δ 2.4 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 7.11 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 7.2–7.5 (m, 5H, ArH); MS m/z (%) 335 (M^++2, 23), 333 (M^+, 0.3), 231 (8), 129 (6), 106 (33), 91 (80), 77 (100). Anal. Calcd. for $C_{18}H_{15}N_5S$ (Mw 333.42): C, 64.84; H, 4.53; N, 21.00. Found: C, 64.46; H, 4.59; N, 21.08%.

3-Phenyl-5-methyl-6-phenylazo-thiazolo[2,3-c][1,2,4]triazole (4Ac): yield 0.35 g (45%), mp 200

°C; ^{1}H NMR (DMSO-d_6) δ 2.3 (s, 3H, CH_3), 7.3–8.0 (m, 10H, ArH); MS m/z (%) 319 (M^+, 1), 205 (1.1), 217 (1.1), 135 (1.4), 108 (2), 90 (3), 77 (13), 65 (13), 50 (100). Anal. Calcd. for $C_{17}H_{13}N_5S$ (Mw 319.39): C, 63.93; H, 4.10; N, 21.93. Found: C, 63.72; H, 3.95; N, 21.75%.

3-Phenyl-5-methyl-6-(p-chlorophenylazo)-thiazolo[2,3-c][1,2,4]-triazole (4Ad): yield 0.61 g (69%), mp 208 °C; ^{1}H NMR (DMSO-d_6) δ 2.6 (s, 3H, CH_3), 7.10–7.40 (m, 5H, ArH), 7.52 (d, 2H, Ar-H), 7.9 (d, 2H, Ar-H); MS m/z (%) 354 (M^++1, 0.2), 353 (M^+, 1), 169 (15), 126 (3), 111 (22), 98 (28), 89 (21), 74 (100); Anal. Calcd. for $C_{17}H_{12}ClN_5S$ (Mw 353.84): C, 57.71; H, 3.42; N, 19.79. Found: C, 52.50; H, 4.00; N, 19.60%.

3-Phenyl-5-methyl-6-(p-nitrophenylazo)-thiazolo[2,3-c][1,2,4]-triazole (4Ae): yield 0.81 g (90%), mp 220 °C; ^{1}H NMR (DMSO-d_6) δ 2.60 (s, 3H, CH_3), 7.4–7.5 (m, 5H, ArH), 7.9 (d, 2H, Ar-H), 8.3 (d, 2H, Ar-H); MS m/z (%) 365 (M^++1, 1.4), 262 (2), 215 (1.5), 172 (1.5), 149 (1.6), 121 (2.6), 108 (8.7), 92 (3.6), 89 (9), 50 (100); Anal. Calcd. for $C_{17}H_{12}N_6O_2S$ (Mw 364.39): C, 56.04; H, 3.32; N, 23.06. Found: C, 55.42; H, 3.34; N, 22.91%.

3-(p-Methoxyphenyl)-5-methyl-6-phenylazo-thiazolo[2,3-c][1,2,4]-triazole (4Ba): yield 0.42 g (48%), mp 208–210 °C; IR (KBr) ν_{max} 1246 (CH_3OC) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.3 (s, 3H, CH_3), 3.85 (s, 3H, $ArOCH_3$), 7.2 (d, 2H, Ar-H), 7.22–7.50 (m, 5H, Ar-H), 8.9 (d, 2H, Ar-H); MS m/z (%) 351 (M^+, 16), 268 (14), 211 (11), 161 (8), 135 (29), 117 (7), 92 (99), 78 (9), 76 (100). Anal. Calcd. for $C_{18}H_{15}N_5OS$ (Mw 349.42): C, 61.87; H, 4.33; N, 20.04. Found: C, 61.66; H, 5.04; N, 19.95%.

3-(p-Methylphenyl)-5-methyl-6-phenylazo-thiazolo[2,3-c][1,2,4]triazole (4Bb): yield 0.25 g (30%), mp 205 °C; ^{1}H NMR (DMSO-d_6) δ 2.4 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 7.00–8.1 (m, 9H, Ar-H); MS m/z (%) 333 (M^+, 02), 248 (0.3), 182 (1), 165 (1), 135 (5), 115 (18), 103 (28), 91 (30), 76 (53). 50 (100). Anal. Calcd. for $C_{18}H_{15}N_5S$ (Mw 333.42): C, 64.84; H, 4.53; N, 21.00. Found: C, 60.50; H, 3.77; N, 20.83%.

3-(p-Chloropheny)l-5-methyl-6-phenylazo-thiazolo[2,3-c][1,2,4]-triazole (4Bd): yield 0.34 g (39%), mp 172–175 °C; ^{1}H NMR (DMSO-d_6) δ 2.4 (s, 3H, CH_3), 7.0–7.6 (m, 9H, ArH); MS m/z (%) 355 (M^++1, 2), 274 (2), 253 (2.2), 217 (2), 170 (2.6), 137 (4), 111 (14), 92 (3), 89 (17), 77 (8), 51 (100); Anal. Calcd. for $C_{17}H_{12}ClN_5S$ (Mw 353.84): C, 57.715 H, 3.42; N, 19.79. Found: C, 57.40; H, 3.56; N, 19.86%.

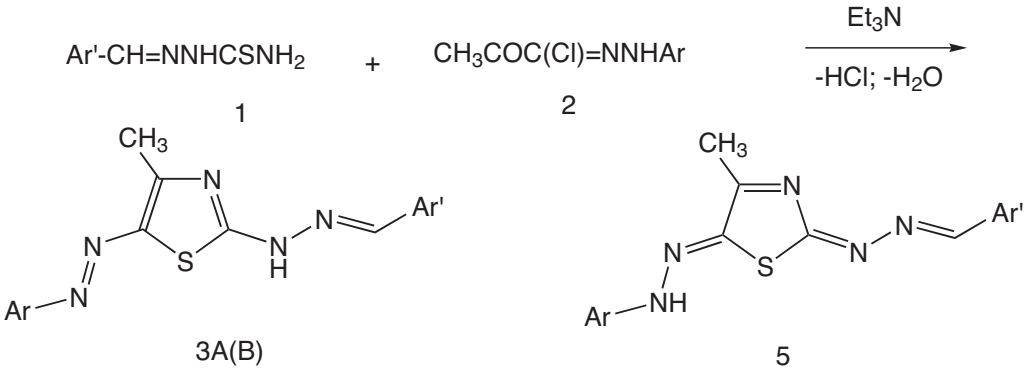
3-(p-Nitrophenyl)-5-methyl-6-phenylazo-thiazolo[2,3-c][1,2,4]-triazole (4Be): yield 0.58 g (64%), mp 210–212 °C; ^{1}H NMR (DMSO-d_6) δ 2.70 (s, 3H, CH_3), 7.4–7.5 (m, 5H, ArH), 8.05 (d, 2H, Ar-H), 8.35 (d, 2H, Ar-H); MS m/z (%) 365 (M^++1, 1.4), 262 (2), 215 (1.5), 172 (1.5), 149 (1.6), 121 (2.6), 108 (8.7), 92 (3.6), 89 (9), 50 (100); Anal. Calcd. for $C_{17}H_{12}N_6O_2S$ (Mw 364.39): C, 56.04; H, 3.32; N, 23.06. Found: C, 55.51; H, 3.43; N, 23.01%.

3. Results and discussion

3.1. Synthesis and characterizations

Treatment of benzaldehyde thiosemicarbazone **1c** with each of the hydrazonoyl chlorides **2a–e** in refluxing ethanol in the presence of triethylamine afforded the respective arylazothiazole derivatives **3Aa–e** (Scheme 1). Similar treatment of substituted benzaldehyde thiosemicarbazones **1a–e** each with the hydrazonoyl chloride **2c** yielded the respective phenylazothiazole derivatives **3Ba–e**. Such reactions seem to follow a pathway similar to that reported for reactions of hydrazonoyl halides with thiourea and thiosemicarbazide, which were reported to yield 5-arylazo derivatives of 2-amino- and 2-hydrazino-thiazole, respectively.[1] The structures of the compounds

3A(B) were elucidated on the basis of their spectral data (MS, IR, ^{1}H NMR, and UV) and elemental analyses (see Experimental). For example, their IR spectra revealed the absence of the C=O absorption bands present in the spectra of the starting hydrazonoyl chlorides **2**. In addition, their ^{1}H NMR spectra in $CDCl_3$ revealed 3 characteristic singlet signals at δ 2.6–2.7 (thiazole-4-CH_3), 7.8–7.9 (CH=N), and 8.6–8.7 (NH). The electronic absorption spectra of compounds **3A(B)** in ethanol (Table 1) showed in each case an intense absorption band in the region 450–485 nm assignable to the arylazo chromophoric group. The spectra of the product **3Ac**, taken as a representative example of the series prepared, in different solvents of different polarity showed little, if any, changes. This finding indicates that the studied compounds **3** exist predominantly in one tautomeric form, namely the indicated azo-hydrazone tautomeric structure **3** (Scheme 1). The other possible tautomeric hydrazono-azine structure **5** (Scheme 1) was thus excluded. This conclusion is further confirmed by the oxidative cyclization of compounds **3A(B)** described below.



Scheme 1.

Table 1. Electronic absorption spectral data of compounds **3A(B)** in ethanol.

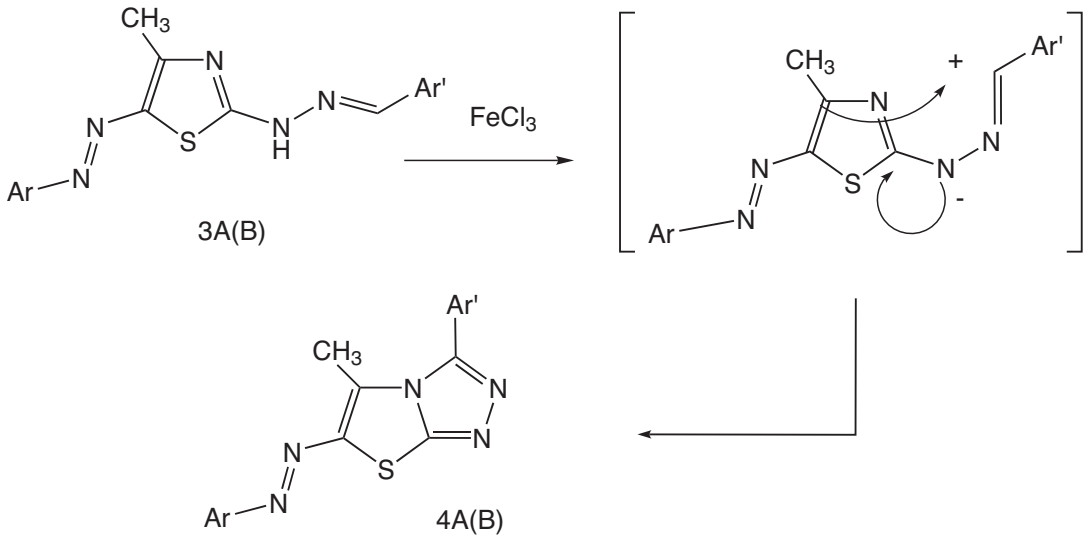
Compd. no.	λ_{max} nm (log ε)	Compd. no.	λ_{max} nm (log ε)
3Aa	479 (4.48), 330 (4.07)	**3Ba**	459 (4.31), 321 (4.75)
3Ab	482 (4.60), 319 (4.18)	**3Bb**	457 (4.49), 316 (4.23)
3Ac[a)]	473 (4.36), 314 (3.96)	**3Bc**	473 (4.36), 314 (3.96)
3Ad	473 (4.20), 311 (3.89)	**3Bd**	461 (4.49), 318 (4.18)
3Ae	655 (4.11), 467 (4.62)	**3Be**	478 (4.19), 335 (4.28)

[a)] Solvent: λ_{max} nm (log ε): n-PrOH: 459 (4.44), 321 (3.99); dioxane: 458 (4.40), 314 (4.08); $HCCl_3$: 456 (4.33), 314 (4.07); MeOH: 471 (4.44), 313 (3.03); MeCN: 441 (4.17), 313 (4.02).

When each of the aldehyde N-(5-arylazo-4-methylthiazol-2-yl)hydrazones **3A(B)** was treated with an equivalent amount of iron(III) chloride in refluxing ethanol for 30 min, it furnished, in each case, one crystalline product as evidenced by TLC analysis. The isolated products proved to be the respective 3-aryl-6-arylazo-5-methyl-thiazolo[2,3-*c*][1,2,4]triazoles **4A(B)** (Scheme 2). Their structures were confirmed by their spectral data (MS, IR, and ^{1}H NMR) and elemental analyses. For example, both the elemental analysis and mass spectrum of each compound revealed that it has 2 hydrogen atoms less than the respective hydrazone **3**. Moreover, their

^{1}H NMR spectra showed the absence of the –N=CH- and hydrazone –NH-N=C proton signals present in the spectra of their precursors **3**.

The conversion of **3** into **4** is considered to proceed via 1,5-electrocyclization of the initially formed nitrilimines (Scheme 2). This suggested pathway is reminiscent of other related oxidative cyclization of aldehyde N-heteroarylhydrazones with iron(III) chloride, which was reported to proceed via initial generation of the respective nitrilimines, which undergo in situ 1,5-electrocyclization to give the respective fused heterocycles.[15,16]



Ar / Ar' : A, XC_6H_4 / Ph; B, Ph / XC_6H_4;
X : a, CH_3O; b, CH_3; c, H; d, Cl; e, O_2N

Scheme 2.

3.2. Solvatochromic properties

The electronic absorption spectra of the azo compounds prepared, **4A(B)**, were recorded at a concentration of 10^{-6} M over the range 300–700 nm using a series of 6 solvents of different polarities, namely 1-propanol, ethanol, dioxane, chloroform, methanol, and acrtonitrile. The results are given in Tables 2 and 3. As shown in these tables, each of the studied compounds exhibits 2 absorption bands in the ranges 320–420 and 450–640 nm in all solvents used. The former UV bands for all of the studied compounds **4A(B)** suffer small solvent shifts, behavior that is expected for local electronic transitions corresponding to $\pi-\pi^*$ transitions. The main visible band displayed by all compounds in the region 430–650 nm is an intense one and is relatively influenced by changing the solvent and the substituent present. For example, the visible spectra of the 2 compounds **4A(B)d** (p-Cl) and **4A(B)e** (p-NO_2) in acetonitrile (Tables 2 and 3) comprise a band appearing at longer wavelengths [550 (549) and 636 (616) nm], respectively, which exceed by far the usual solvent shift. This behavior seems to indicate that such dyes may be liable to form a solvated complex.[17–19]

Next, the effects of solvent polarity/polarizability and hydrogen bonding property on the absorption spectra of the studied compounds **4A**(**B**) were evaluated by means of the linear solvation energy relationship (LSER), namely the Kamlet–Taft equation (Eq. (1)):[11,12]

Table 2. Electronic absorption spectral data of compounds **4Aa–e** in various solvents.

Compd. no.	Solvent: λ_{max} nm (log ε)	Compd. no.	Solvent: λ_{max} nm (log ε)
4Aa	n-PrOH**:** 459 (4.10), 330 (409); EtOH: 456 (4.09), 325 (4.04); Dioxane: 430 (3.99), 343 (4.05); $HCCl_3$: 426 (4.06), 326 (4.00); MeOH: 430 (4.38), 304 (4.13); MeCN: 422 (3.99), 330 (4.07).	**4Ad**	n-PrOH: 459 (4.27), 320 (4.18); EtOH: 458 (4.22), 320 (4.06); Dioxane: 445 (4.28), 313 (4.10); $HCCl_3$: 439 (4.32), 321 (4.19); MeOH: 455 (4.19), 304 (4.11); MeCN: 550 (3.92), 435 (4.12).
4Ab	n-PrOH : 466 (4.24), 325 (4.02); EtOH: 464 (4.25), 320 (3.92); Dioxane: 452 (4.21), 316 (3.91); $HCCl_3$: 449 (4.04), 323 (3.81); MeOH: 459 (3.98), 308 (3.90); MeCN: 425 (3.62), 325 (3.83).	**4Ae**	n-PrOH: 453 (4.24), 345 (4.13); EtOH: 453 (4.24), 310 (4.05); Dioxane: 442 (4.27), 382 (4.15); $HCCl_3$: 443 (4.17), 337 (3.95); MeOH: 448 (4.20), 382 (4.10); MeCN: 636 (4.08), 434 (4.15).
4Ac	n-PrOH: 449 (4.02), 329 (4.11); EtOH: 452 (3.97), 325 (3.99); Dioxane: 439 (4.08), 329 (4.09); $HCCl_3$: 422 (4.01), 325 (4.00); MeOH: 452 (3.97), 319 (3.98); MeCN: 423 (4.02), 333 (4.08).		

Table 3. Electronic absorption spectral data of compounds **4Ba–e** in various solvents.

Compd. no.	Solvent: λ_{max} nm (log ε)	Compd. no.	Solvent: λ_{max} nm (log ε)
4Ba	n-PrOH: 461 (4.09), 329 (4.16); EtOH: 460 (4.08), 331 (4.17); Dioxane: 450 (3.96), 325 (4.03); $HCCl_3$: 439 (4.07), 328 (4.17); MeOH: 457 (4.05), 325 (4.15); MeCN: 430 (3.99), 323 (4.15).	**4Bd**	n-PrOH: 460 (4.11), 324 (4.11); EtOH: 457 (4.11), 323 (4.12); Dioxane: 446 (4.16), 325 (4.19); $HCCl_3$: 439 (4.09), 323 (4.10); MeOH: 456 (4.11), 325 (4.13); MeCN: 549 (3.84), 409 (4.03).
4Bb	n-PrOH: 460 (4.09), 323 (4.08); EtOH: 456 (4.09), 323 (4.11); Dioxane: 447 (4.10), 325 (4.12); $HCCl_3$: 438 (4.06), 329 (4.06); MeOH: 454 (4.09), 320 (4.12); MeCN: 425 (4.02), 383 (4.12).	**4Be**	n-PrOH: 482 (4.40), 346 (4.19); EtOH: 478 (4.42), 346 (4.21); Dioxane: 467 (4.39), 337 (4.22); $HCCl_3$: 466 (4.37), 338 (4.25); MeOH: 474 (4.43), 340 (425); MeCN: 616 (4.24), 330 (4.13).
4Bc	n-PrOH: 449 (4.02), 329 (4.11); EtOH: 452 (3.97), 320 (3.99); Dioxane: 439 (4.08), 329 (4.09); $HCCl_3$: 422 (4.01), 325 (4.00); MeOH: 452 (3.97), 319 (3.98); MeCN: 423 (4.02), 333 (4.08).		

$$\upsilon = \upsilon^o + s\pi * + b\beta + a\alpha \quad (1)$$

where $\pi*$ is the measure of solvent dipolarity/polarizabilty, β is the scale of the solvent hydrogen bond acceptor (HBA) basicities, α is the scale of the solvent hydrogen-bond donor (HBD) acidities, and υ^o is the regression value of the solute property in the reference solvent cyclohexane. The values of such solvent parameters are given in Table 4. The regression coefficients s, b, and a in Eq. (1) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequencies) to the indicated solvent parameters. The values

of these regression coefficients were obtained by means of multiple linear regression analysis. The results are depicted in Table 5. The values (0.985–0.921) of the correlation coefficients R indicate that the spectroscopic data are fairly correlated by Eq. (1). The negative sign of a given regression coefficient indicates that the energy of the electronic transition is decreased by the corresponding solvent property and vice versa.

The percentage contributions of the solvatochromic parameters π^*, β, and α for the studied compounds are given in Table 6. As shown, the changes in the spectra of the studied compounds are more influenced by dipolarity/polarizability than the H-bonding character of the solvents used. This influence is increased by both electron-donating and electron-withdrawing substituents.

Table 4. Solvent parameters.[12]

Solvent	$\pi*$	β	α
1-Propanol	0.47	0.88	0.79
Ethanol	0.54	0.77	0.83
Dioxane	0.55	0.37	0.0
Chloroform	0.58	0.0	0.44
Methanol	0.60	0.62	0.93
Acetonitrile	0.75	0.31	0.19

Table 5. Regression fits to solvatochromic parameters (Eq. (1)).

Compound no.	υ_o (10^3 cm^{-1})	s	b	a	R[a]	±S[b]
4Aa	21.29	4.02	–1.38	–0.050	0.932	0.453
4Ab	18.85	6.27	–0.043	–0.668	0.976	0.263
4Ac	22.72	1.659	–1.518	–0.316	0.921	0.452
4Ad	33.186	–18.321	–3.397	1.216	0.931	0.965
4Ae	38.895	–28.726	–4.072	1.955	0.926	1.610
4Ba	20.815	3.51	–0.911	–0.264	0.957	0.294
4Bb	19.341	5.561	0.225	–0.691	0.985	0.175
4Bc	22.72	1.659	–1.518	–0.316	0.921	0.452
4Bd	33.029	–18.093	–3.395	1.240	0.933	0.944
4Be	35.622	–25.357	–4.207	2.379	0.932	1.399

[a] Correlation coefficient; [b] standard error of the estimate

Table 6. Contribution percentages of solvatochromic parameters.

Compound no.	$\rho\pi^*$ (%)	$\rho\beta$ (%)	$\rho\alpha$ (%)
4Aa	73.76	25.32	0.01
4Ab	89.80	0.006	9.57
4Ac	47.50	43.40	9.05
4Ad	79.88	14.82	5.30
4Ae	82.66	11.71	5.62
4Ba	74.92	19.44	5.63
4Bb	85.85	3.47	10.67
4Bc	47.50	43.40	9.05
4Bd	79.61	14.94	5.46
4Be	79.38	13.17	7.45

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