

Synthesis and antibacterial studies of azodispersed dyes derived from 2-(thiazol-2-yl)phthalazine-1,4-diones

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Abstract A dibenzobarrelene derivative was used as key intermediate for the synthesis of 2-(4-(methyl/phenyl)thiazol-2-yl)-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzotriazolophthalazine-1,4-diones. These compounds were coupled with the appropriate diazonium chlorides to give the corresponding 5-(aryloxy)thiazole derivatives. The synthesized dyes were applied to polyester as disperse dyes, and their antibacterial, color measurement, and fastness properties were evaluated.

Keywords Thiazole · Azodispersed dyes · Polyester fabrics · Antibacterial · Color measurements · Fastness properties

Introduction

Thiazoles and their derivatives have attracted continued interest over the years because of their various biological activities [1, 2]. Recently they have found application in drug development for treatment of allergies [3], hypertension [4], inflammation [5], as central nervous system (CNS) depressant [6, 7], bacterial [8] and human immune-deficiency virus (HIV) infections [9], pain [10], as fibrinogen receptor antagonists with antithrombotic activity [11], and as new inhibitors of bacterial DNA gyrase B [12].

On the other hand, the class of phthalazines possesses a broad spectrum of biological effectiveness such as antibacterial [13–15], anticonvulsant [16], cardiotoxic [17], and vasorelaxant [18] activities. In view of the above biological importance, in continuation of our studies on the chemistry of 2-(4-(methyl/phenyl)thiazol-2-yl)-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzotriazolophthalazine-1,4-diones **3** [13], and as part of our program directed towards developing new approaches to a variety of heterocycles incorporating the thiazole moiety [13, 14, 19] of expected potential activity, we now report on the successful synthesis of some new 2-[5-(aryloxy)-4-substituted-thiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzotriazolophthalazine-1,4-diones **4a–4n** starting from dibenzobarrelene **1** [20] and their application as disperse dyes for dyeing polyester fabrics.

Results and discussion

Coupling of **3a** and **3b** with various aryldiazonium chlorides in pyridine afforded the corresponding 4-substituted 5-(aryloxy)thiazole derivatives **4a–4n**. The spectral data of **4a–4n** were consistent with their structure. Their infrared (IR) spectra showed bands at $\bar{\nu} = 3,360\text{--}3,196$ (NH), $1,736\text{--}1,702$ (CO), and $1,530\text{--}1,506\text{ cm}^{-1}$ (N=N). ^1H nuclear magnetic resonance (NMR) of **4b** showed signals at $\delta = 2.35$ (s, 3H, CH₃), 2.45 (s, 3H, CH₃-tolyl), and $7.1\text{--}7.6$ (m, 12H, Ar-H) ppm. Also, the ^1H NMR spectrum of **4c** revealed two singlet signals at $\delta = 2.4$ and 3.85 ppm corresponding to CH₃ and OCH₃ groups, in addition to two doublet signals at $\delta = 6.9$ and 7.7 ppm due to four protons of the *p*-substituted aryloxy moiety and multiplet signals at $7.1\text{--}7.4$ ppm due to eight aromatic protons. Moreover, the ^1H NMR spectrum of **4i** revealed among the characteristic signals a singlet at $\delta = 2.4$ ppm due to CH₃ protons, in

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addition to two doublet signals at $\delta = 7.1$ and 8.1 ppm due to four protons of the *p*-substituted arylazo moiety and multiplet signals at $\delta = 7.2$ – 7.6 ppm due to 13 aromatic protons.

Furthermore, the ^1H NMR spectrum of **4i** showed multiplet signals at $\delta = 7.1$ – 8.0 ppm due to 17 aromatic protons. In addition, the ^1H NMR spectrum of **4n** revealed signals at $\delta = 1.4$ (t, 3H, CH_3), 3.9 (q, 2H, CH_2O), and 7.1–7.6 (m, 17H, Ar–H) ppm. As an example, the ESI(+) mass spectrum of **4c** showed three quasimolecular ion peaks at 522 ($[\text{M} + \text{H}]^+$), 544 ($[\text{M} + \text{Na}]^+$), and 1064 ($[\text{2M} - \text{H} + \text{Na}]^+$), and the ESI(–) mass spectrum showed one quasimolecular ion peak at 520 ($[\text{M} - \text{H}]^-$) pointing at 521 as the molecular mass of the compound (Scheme 1).

Dyeing of polyester fabrics and dyeing properties

Color measurement

The effect of the nature of different substituents on dyeing behavior, color hue, and depth was investigated. This investigation depends on some spectral data of the dyed materials. The most commonly used function $f(R)$ is that developed theoretically by Kubelka and Munk. In their theory, the optical properties of a sample are described by two values: K is the measure of the light absorption, and

S is a measure of the light scattering. On textiles, K is determined primarily by the dyestuffs and S only by the substrate. From the wavelength, Kubelka and Munk calculate Eq. (1) for the reflectance R of thick, opaque samples with the constants of K and S :

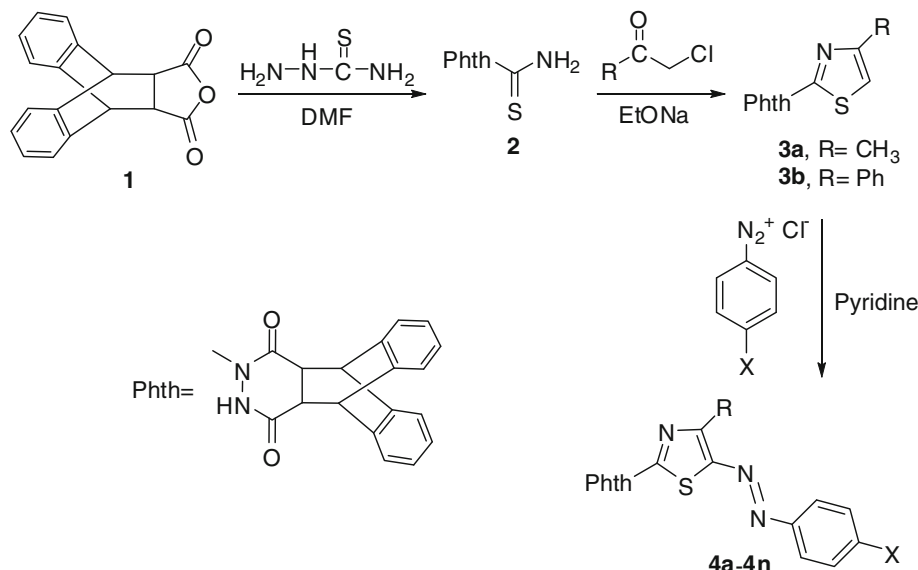
$$K/S = (1 - R)^2/2R. \quad (1)$$

In this equation R is used as a ratio, e.g., 32% reflectance as 0.32. The K/S value at λ_{max} was taken as a measure of color depth.

On the other hand, the psychometric coordinates (L^* , a^* , b^*) for each dyed sample were obtained to illustrate the color hues, where L^* is the lightness, ranging from 0 to 100 (0 for black and 100 for white); a^* is the red-green axis, (+) for red, zero for grey, and (–) for green; and b^* is the yellow-blue axis, (+) for yellow, zero for grey, and (–) for blue.

The parent dyestuff in each group is taken as the standard in color difference calculation (ΔL^* , ΔC^* , ΔH^* , and ΔE) [21–23]. The results are measured using CIE-LAB techniques and given in Table 1, where ΔL^* is the lightness difference, ΔC^* the chroma difference, ΔH^* the hue difference, and ΔE the total color difference. A negative sign of ΔL^* indicates that the dyed fiber becomes darker than the standard, but a positive sign indicates that the dyed fiber becomes lighter than the standard. A negative sign of

Scheme 1



	R	X		R	X
4a	CH_3	H	4h	Ph	H
4b	CH_3	CH_3	4i	Ph	CH_3
4c	CH_3	OCH_3	4j	Ph	OCH_3
4d	CH_3	Cl	4k	Ph	Cl
4e	CH_3	Br	4l	Ph	Br
4f	CH_3	NO_2	4m	Ph	NO_2
4g	CH_3	COOEt	4n	Ph	COOEt

Table 1 Optical measurements of compounds **4a–4n**

Dye	R%	a^*	b^*	L^*	C^*	H^*	ΔL^*	ΔC^*	ΔH^*	ΔE^*	K/S
4a	5.63	8.28	28.63	51.09	29.71	1.29	–	–	–	–	7.91
4b	7.33	7.58	24.6	53.48	25.74	1.27	2.39	–3.97	–0.02	4.63	5.86
4c	8.0	5.66	35.9	62.14	36.35	1.42	11.05	6.64	0.13	12.89	5.29
4d	5.28	8.6	31.3	53.2	32.52	1.3	2.11	2.81	0.01	3.51	8.5
4e	2.85	9.82	42.55	48.58	43.67	1.34	–2.51	13.96	0.05	14.18	16.56
4f	3.88	11.63	21.79	44.37	24.7	1.08	–6.72	–5.01	–0.21	8.38	11.91
4g	5.3	15.71	23.78	47.4	28.5	0.99	–3.69	–1.21	–0.3	3.89	8.46
4h	6.1	20.26	57.61	66.11	61.08	1.23	–	–	–	–	7.20
4i	2.6	25.12	63.15	57.14	68.3	1.19	–8.97	7.22	–0.04	11.51	18.24
4j	4.77	20.19	59.2	63.01	62.56	1.24	–3.1	1.48	–0.01	3.43	9.51
4k	2.08	29.13	63.5	53.46	69.85	1.14	–12.6	8.77	–0.09	15.41	23.05
4l	2.95	27.21	68.46	62.17	73.68	1.19	–3.94	12.6	–0.04	13.2	15.96
4m	4.88	21.84	35.43	48.76	41.62	1.02	–17.3	–19.46	–0.21	26.07	9.27
4n	7.12	25.01	49.53	61.96	55.49	1.1	–4.15	–5.59	–0.13	6.96	6.06

R reflectance; a^* red-green axis; b^* yellow-blue axis; L^* lightness; C^* chroma; H^* hue; ΔL^* lightness difference; ΔC^* chroma difference; ΔH^* hue difference; ΔE total color difference

ΔC^* indicates that the dyed fiber becomes duller than the standard, but a positive sign indicates that the dyed fiber becomes brighter than the standard. A negative sign of ΔH^* indicates that the color directed to red color, while a positive sign indicates that the color directed to yellowish.

The values of K/S of **4a–4n** vary from 5.29 to 23.05. The introduction of methyl, methoxy, chloro, bromo, and nitro groups in dyes **4d**, **4e**, **4f**, **4g**, **4i**, **4j**, **4k**, **4l**, and **4m** increases the strength of K/S values and deepens the color compared with the parent dyes **4a** and **4h** (Table 1).

The replacement of the methyl by a phenyl group in the thiazole moiety decreases the value of K/S, indicating that the dyes **4h–4n** show higher affinity towards dyeing of polyester fabrics than **4a–4g**. Dyes **4c–4e** and **4i–4l** with positive ΔC values are brighter than the parent dyes **4a** and **4h**, while the other dyes are duller than the parent dyes. Dyes **4b–4d** with positive ΔL^* values are lighter than the parent dye **4a**, while the other dyes with negative ΔL^* are darker than the parent. The positive value of a^* and b^* indicates that all groups shift the color hues of the dye to reddish direction on the red-green axis and to the yellowish direction in the yellow-blue axis, respectively.

Assessment of color fastness

Most influences that can affect fastness are light, washing, heat, perspiration, and atmospheric pollution. Conditions of such tests are chosen to correspond closely to treatments employed in manufacture and ordinary use conditions [24]. Results are given after usual matching of tested samples against standard reference (the grey scale) [24]. The results revealed that these dyes have good fastness properties (Table 2).

Antibacterial activity

Fourteen compounds were screened in vitro for their antibacterial activity against two strains of bacteria, *Bacillus thuringiensis* and *Escherichia coli*, by the agar diffusion technique [25]. A 2 mg/cm³ solution in dimethyl sulfoxide (DMSO) was used. The bacteria were maintained on nutrient agar. DMSO showed no inhibition zones. The agar media were incubated with different microorganism cultures tested. After 24 h of incubation at 30 °C, the diameter of inhibition zone (mm) was measured (Table 3). Ampicillin and chloramphenicol were used at concentration of 2 mg/cm³ as references.

The results presented in Table 3 reveal that compounds **4a**, **4c**, **4k**, **4l**, and **4m** exhibited interestingly high activities compared with the reference chemotherapeutics against both *B. thuringiensis* and *E. coli*. Compounds **4a**, **4d**, **4e**, **4f**, **4g**, **4i**, **4j**, and **4n** exhibited high activity against *B. thuringiensis* and moderate activity against *E. coli*. In general, the compounds under investigation show more significant activities against *B. thuringiensis* than against *E. coli*. In conclusion, we report herein a simple and convenient route for the synthesis of some new azo dyes based on phthalazine with antibacterial activities.

Conclusions

Fourteen useful disperse dyes **4a–4n** were synthesized by azo coupling and were investigated for their dyeing characteristic on polyester, and showed good light, washing, heat, and acid perspiration fastness with antibacterial activities. The remarkable degree of brightness after

Table 2 Fastness properties of compounds **4a–4n**

Dye	Washing, 75 °C	Rubbing		Sublimation		Acid perspiration	Light, 4 h
		Dry	Wet	180 °C	210 °C		
4a	4	2–3	3–4	3	2–3	4	4
4b	4	2–3	3–4	3–4	2–3	3–4	5
4c	4	2–3	2–3	3–4	2–3	4	2–3
4d	4	2–3	2–3	4	3	4	4
4e	4–5	2–3	3–4	3–4	2–3	3–4	6
4f	4	2–3	3–4	3–4	2–3	3–4	4
4g	4	2–3	4–5	4	3	4	2–3
4h	4–5	2–3	3–4	2–3	1–2	4	2–3
4i	4–5	4–5	4–5	2–3	1–2	4	4
4j	4–5	2–3	3–4	3–4	2–3	4	2–3
4k	4–5	2–3	3–4	2–3	1–2	3–4	4
4l	4	2–3	4	4	2–3	3–4	4
4m	4	4	4	3–4	2–3	3–4	6
4n	4	2–3	4	4–5	3–4	4–5	2–3

Table 3 Inhibition zone (mean diameter of inhibition/mm) as a criterion of antibacterial activity of the newly synthesized compounds (2 mg/cm³ solution in DMSO)

Compound	Inhibition zone (mm)	
	<i>B. thuringiensis</i> (Gram positive)	<i>E. coli</i> (Gram negative)
4a	30	14
4b	25	20
4c	30	20
4d	30	10
4e	35	15
4f	25	15
4g	30	15
4h	15	20
4i	40	–
4j	30	15
4k	33	20
4l	35	20
4m	30	20
4n	43	10
Ampicillin	18	19
Chloramphenicol	23	19

washings is an indication of good penetration and the excellent affinity of these dyes for the fabric due to the accumulation of polar groups.

Experimental

All melting points were determined on a Gallenkamp electric melting point apparatus. Thin-layer chromatography (TLC)

analysis was carried out on silica gel 60 F₂₅₄ precoated aluminum sheets. Infrared spectra were recorded on FTIR 5300 Spectrometer and Perking Elmer Spectrum RXIFT-IR System at the Faculty of Science, El-Azhar University, using the potassium bromide wafer technique. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer using the indicated solvents and tetramethylsilane (TMS) as an internal reference at the Georgia State University, Atlanta, GA and on a Varian XL 200 MHz, at the Microanalytical Center of Cairo University. Mass spectra were recorded on ESI MS with Quattro Triple Quadruple Mass Finigan MAT-Incos 50 ESILCQ (Finigan) at the Georg-August University Goettingen, Germany. Elemental analyses (C, H, N) were carried out at the micro-analytical Center of Cairo University, Giza, Egypt. The elemental analyses were found to agree favorably with the calculated values. The dyeing assessment, fastness tests, and color measurements were carried out at El-Nasr Company for Spinning and Weaving, El-Mahalla, El-Kubra, Egypt.

The syntheses of dibenzobarrelene **1** [20], thioamide **2** [26], and the thiazole derivatives **3a** and **3b** [13] were conducted according to known procedures.

Synthesis of 2-[5-(arylo)-4-substituted-thiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenbenzo-[g]phthalazine-1,4-diones **4a–4n**

A well-stirred solution of aromatic amine (5 mmol) in 1.2 cm³ conc. HCl and 2 cm³ H₂O was cooled in an ice bath and diazotized with the solution of 0.345 g NaNO₂ (5 mmol) in 2 cm³ H₂O. The cold diazonium solution was added slowly to a well-stirred solution of 1.937 g **3a** or 2.248 g **3b** (5 mmol) in 15 cm³ pyridine. The reaction mixture was stirred for another 2 h. The crude product was

filtered off, thoroughly dried, and recrystallized from a suitable solvent to give **4a–4n**.

2-[4-Methyl-5-(phenylazo)thiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4a**, C₂₈H₂₁N₅O₂S)

Crystallization from EtOH-benzene afforded 1.97 g (80%) **4a**, reddish brown. M.p.: 248 °C; IR (KBr): $\bar{\nu}$ = 3,220 (NH), 1,770, 1,696 (CO), 1,506 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.4 (s, 3H, CH₃), 3.4 (s, 2H, C11-H, C12-H), 4.9 (s, 2H, C9-H, C10-H), 7.0–7.7 (m, 13H, Ar-H), 12.0 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 172.1, 169.4, 142.6, 139.6, 129.3, 128.8, 127.6, 126.8, 125.5, 124.7, 108.3, 45.0, 40.8, 20.5 ppm.

2-[4-Methyl-5-(4-methylphenylazo)thiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4b**, C₂₉H₂₃N₅O₂S)

Crystallization from EtOH-benzene afforded 2.33 g (92%) **4b**, orange. M.p.: 304 °C; IR (KBr): $\bar{\nu}$ = 3,128 (NH), 1,714 (CO), 1,512 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.35 (s, 3H, CH₃-C₆H₄), 2.45 (s, 3H, CH₃), 3.3 (s, 2H, C11-H, C12-H), 4.8 (s, 2H, C9-H, C10-H), 7.1–7.6 (m, 12H, Ar-H), 11.9 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.6, 171.4, 169.0, 145.3, 140.0, 138.5, 138.4, 129.5, 127.0, 126.8, 126.0, 125.1, 124.2, 104.4, 45.2, 43.5, 21.4, 20.1 ppm.

2-[5-(4-Methoxyphenylazo)-4-methylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4c**, C₂₉H₂₃N₅O₃S)

Crystallization from DMF-H₂O afforded 2.217 g (85%) **4c**, reddish brown. M.p.: 245 °C; IR (KBr): $\bar{\nu}$ = 3,225 (NH), 1,706 (CO), 1,509 (N=N) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ = 2.4 (s, 3H, CH₃), 3.3 (s, 2H, C11-H, C12-H), 3.85 (s, 3H, OCH₃), 4.85 (s, 2H, C9-H, C10-H), 6.9 (d, 2H, Ar-H), 7.1–7.4 (m, 8H, Ar-H), 7.7 (d, 2H, Ar-H), 10.3 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 172.3, 171.9, 168.8, 142.6, 139.6, 128.8, 127.6, 126.7, 125.5, 124.6, 115.1, 56.0, 45.1, 40.8, 20.6 ppm; ESI (+) MS: *m/z* = 522 ([M + H]⁺), 544 ([M + Na]⁺), 1064 ([2 M - H + Na]⁺); ESI (-) MS: *m/z* = 520 ([M - H]⁻).

2-[5-(4-Chlorophenylazo)-4-methylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4d**, C₂₈H₂₀ClN₅O₂S)

Crystallization from DMF-MeOH afforded 2.183 g (83%) **4d**, orange. M.p.: 286 °C; IR (KBr): $\bar{\nu}$ = 3,250 (NH), 1,712 (CO), 1,508 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.3 (s, 3H, CH₃), 3.3 (s, 2H, C11-H, C12-H), 4.9 (s, 2H, C9-H, C10-H), 7.0–7.9 (m, 12H, Ar-H), 12.2 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.1, 171.3, 168.7, 148.5, 141.1, 139.0, 134.5, 130.0,

128.9, 127.1, 126.9, 126.7, 126.4, 125.1, 124.1, 103.6, 45.5, 42.3, 19.8 ppm.

2-[5-(4-Bromophenylazo)-4-methylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4e**, C₂₈H₂₀BrN₅O₂S)

Crystallization from DMF-MeOH afforded 2.054 g (72%) **4e**, reddish brown. M.p.: 295 °C; IR (KBr): $\bar{\nu}$ = 3,208 (NH), 1,760, 1,698 (CO), 1,520 (N=N) cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.5 (s, 3H, CH₃), 3.2 (s, 2H, C11-H, C12-H), 4.8 (s, 2H, C9-H, C10-H), 7.2–7.6 (m, 12H, Ar H), 10.9 (br, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 171.9, 171.1, 168.9, 142.5, 139.6, 132.8, 128.5, 126.8, 125.5, 124.7, 106.4, 45.0, 40.8, 20.1 ppm.

2-[4-Methyl-5-(4-nitrophenylazo)thiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4f**, C₂₈H₂₀N₆O₄S)

Crystallization from DMF-MeOH afforded 2.039 g (76%) **4f**, brown. M.p.: 263 °C; IR (KBr): $\bar{\nu}$ = 3,216 (NH), 1,702 (CO), 1,514 (N=N), 1332 (NO₂) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.25 (s, 3H, CH₃), 3.35 (s, 2H, C11-H, C12-H), 4.85 (s, 2H, C9-H, C10-H), 7.1–7.9 (m, 12H, Ar-H), 12.3 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 176.4, 174.8, 169.0, 149.6, 147.2, 141.0, 139.4, 135.2, 129.8, 126.9, 126.8, 125.7, 124.3, 103.6, 46.6, 45.4, 18.9 ppm.

Ethyl 4-[2-(3,4,4a,5,10,10a-hexahydro-1,4-dioxo-5,10-benzenobenzog[phthalazin-2(1H)-yl]-4-methylthiazol-5-ylazo]benzoate (**4g**, C₃₁H₂₅N₅O₄S)

Crystallization from EtOH afforded 1.945 g (69%) **4g**, red. M.p.: 241 °C; IR (KBr): $\bar{\nu}$ = 3,240 (NH), 1,706 (br, CO), 1,514 (N=N) cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.3 (t, 3H, CH₃, *J* = 7.2), 2.6 (s, 3H, CH₃), 3.4 (s, 2H, C₁₁-H, C₁₂-H), 4.3 (q, 2H, CH₂, *J* = 7.2), 4.9 (s, 2H, C₉-H, C₁₀-H), 7.1–7.9 (m, 12H, Ar H), 11.1 (br, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 171.1, 169.6, 165.8, 150.1, 142.3, 139.9, 128.6, 127.4, 126.8, 125.5, 124.7, 102.1, 60.9, 45.1, 40.8, 21.3, 14.7 ppm.

2-[4-Phenyl-5-(phenylazo)thiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[phthalazine-1,4-dione (**4h**, C₃₃H₂₃N₅O₂S)

Crystallization from EtOH-benzene afforded 1.938 g (70%) **4h**, orange. M.p.: 287 °C; IR (KBr): $\bar{\nu}$ = 3,360 (NH), 1,734 (CO), 1,528 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 3.3 (s, 2H, C11-H, C12-H), 4.8 (s, 2H, C9-H, C10-H), 7.2–7.6 (m, 18H, Ar-H), 11.3 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.2, 171.4, 170.1, 169.4, 150.3, 142.5, 139.6, 130.0, 129.0, 129.8, 127.4, 127.2, 126.8, 125.6, 125.0, 124.7, 124.6, 105.1, 45.2, 40.8 ppm.

2-[5-(4-Methylphenylazo)-4-phenylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[*g*]-phthalazine-1,4-dione (**4i**, C₃₄H₂₅N₅O₂S)

Crystallization from EtOH-benzene afforded 2.413 g (85%) **4i**, orange. M.p.: 290 °C; IR (KBr): $\bar{\nu}$ = 3,220 (NH), 1,736 (CO), 1,530 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 2.4 (s, 3H, CH₃), 3.4 (s, 2H, C11-H, C12-H), 4.9 (s, 2H, C9-H, C10-H), 7.1 (d, 2H, Ar-H), 7.2–7.6 (m, 13H, Ar-H), 8.1 (d, 2H, Ar-H), 10.8 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 172.4, 171.5, 169.4, 142.4, 139.5, 138.8, 130.6, 129.0, 127.7, 126.8, 125.6, 125.1, 124.7, 124.6, 122.5, 105.2, 44.9, 40.8, 21.4 ppm; ESI (+) MS: *m/z* = 568 ([M + H]⁺), 590 ([M + Na]⁺), 1,156.9 ([2 M + Na]⁺); ESI (–) MS: *m/z* = 566 ([M-H][–]).

2-[5-(4-Methoxyphenylazo)-4-phenylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[*g*]-phthalazine-1,4-dione (**4j**, C₃₄H₂₅N₅O₃S)

Crystallization from EtOH-benzene afforded 2.539 g (87%) **4j**, orange. M.p.: 260 °C; IR (KBr): $\bar{\nu}$ = 3,226 (NH), 1,726 (CO), 1,534 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 3.3 (s, 2H, C11-H, C12-H), 4.1 (q, 2H, OCH₃), 4.9 (s, 2H, C9-H, C10-H), 7.9–8.0 (m, 17H, Ar-H), 11.0 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.0, 171.9, 168.5, 149.5, 142.9, 139.5, 133.2, 129.4, 129.1, 129.0, 127.7, 127.6, 126.8, 125.8, 124.6, 108.1, 56.0, 45.1, 42.8 ppm.

2-[5-(4-Chlorophenylazo)-4-phenylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[*g*]-phthalazine-1,4-dione (**4k**, C₃₃H₂₂ClN₅O₂S)

Crystallization from EtOH-benzene afforded 2.646 g (90%) **4k**, red. M.p.: 258 °C; IR (KBr): $\bar{\nu}$ = 3,310 (NH), 1,730 (CO), 1,508 (N=N) cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 3.3 (s, 2H, C11-H, C12-H), 4.8 (s, 2H, C9-H, C10-H), 7.2–7.7 (m, 17H, Ar H), 11.0 (br, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.2, 171.3, 169.2, 142.5, 139.5, 129.8, 127.6, 126.8, 125.5, 124.7, 104.1, 45.0, 40.8 ppm.

2-[5-(4-Bromophenylazo)-4-phenylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[*g*]-phthalazine-1,4-dione (**4l**, C₃₃H₂₂BrN₅O₂S)

Crystallization from EtOH-benzene afforded 2.625 g (83%) **4l**, orange. M.p.: 230 °C; IR (KBr): $\bar{\nu}$ = 3,300 (NH), 1,734 (CO), 1,510 (N=N) cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆): δ = 3.47 (s, 2H, C11-H, C12-H), 4.87 (s, 2H, (C9-H, C10-H), 7.1–8.0 (m, 17H, Ar-H), 11.0 (br, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 172.5, 171.4, 169.1, 150.5, 142.0, 139.3, 133.4, 132.6, 129.6, 128.9, 128.8, 127.6, 126.8, 125.5, 124.3, 106.4, 46.0, 44.8 ppm.

2-[5-(4-Nitrophenylazo)-4-phenylthiazol-2-yl]-2,3,4a,5,10,10a-hexahydro-5,10-benzenobenzog[*g*]-phthalazine-1,4-dione (**4m**, C₃₃H₂₂N₆O₄S)

Crystallization from EtOH-benzene afforded 2.395 g (80%) **4m**, red. M.p.: 303 °C; IR (KBr): $\bar{\nu}$ = 3,196 (NH), 1,707 (CO), 1,560, 1,494, 1,332 (N=N, NO₂) cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 3.4 (s, 2H, C11-H, C12-H), 4.9 (s, 2H, C9-H, C10-H), 7.1–8.3 (m, 17H, Ar-H), 11.4 (br, 1H, NH) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 173.2, 170.6, 169.5, 151.3, 147.9, 142.4, 134.8, 129.1, 127.5, 126.8, 125.5, 124.7, 123.9, 104.0, 45.0, 40.8 ppm.

Ethyl 4-[2-(3,4,4a,5,10,10a-hexahydro-1,4-dioxo-5,10-benzenobenzog[*g*]phthalazin-2(1H)-yl)-4-phenylthiazol-5-ylazo]benzoate (**4n**, C₃₆H₂₇N₅O₄S)

Crystallization from EtOH afforded 2.253 g (72%) **4n**, red. M.p.: 286 °C; IR (KBr): $\bar{\nu}$ = 3,250 (NH), 1,714, 1,650 (CO), 1,508 (N=N) cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ = 1.4 (t, 3H, CH₃), 3.4 (s, 2H, C11-H, C12-H), 3.9 (q, 2H, CH₂), 4.9 (s, 2H, C9-H, C10-H), 7.1–7.6 (m, 17H, Ar-H), 10.6 (br, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 174.1, 171.6, 165.8, 150.3, 142.0, 139.9, 133.5, 129.8, 129.3, 128.8, 127.8, 127.0, 126.7, 125.5, 124.8, 104.1, 61.5, 45.1, 44.8, 15.3 ppm.

Dyeing procedures

Preparation of dye dispersion

The required amount of dye (2% shade) was dissolved in DMF and added dropwise with stirring to a solution of Dekol-N (2 g/dm³), an anionic dispersing agent of BASF, then the dye was precipitated in a fine dispersion ready for use in dyeing.

Dyeing of polyester at 130 °C under pressure using Levegal PT (carrier of Bayer)

The dye bath (1:20 liquor ratio), containing 5 g/dm³ Levegal PT (Bayer) as carrier, 4% ammonium sulfate, and acetic acid at pH 5.5, was brought to 60 °C, the polyester fabric was entered and run for 15 min. The fine dispersion of the dye (2%) was added, and the temperature was raised to boiling within 45 min, dyeing was continued at boiling temperature for about 1 h, then the dyed material was rinsed and soaped with 2% nonionic detergent to improve rubbing and wet fastness.

Assessment of color fastness (Table 2)

Fastness to washing, perspiration, light, and sublimation was tested according to the reported methods.

Fastness to washing

A specimen of dyed polyester fabric was stitched between two pieces of undyed cotton fabric, all of equal diameter, 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, and 5-excellent.

Fastness to perspiration

The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of undyed cotton fabric, all of equal diameter, and then immersing in the acid medium 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, and 5-excellent. The acid solution (pH 3.5) contained sodium chloride 10 g/dm³, lactic acid 1 g/dm³, disodium orthophosphate 1 g/dm³, and histidine monohydrochloride 0.25 g/dm³.

Fastness to rubbing

The dyed polyester fabric was placed on the base of crockmeter (Atlas electronic type), 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 20 times by making ten complete turns of the crank. For wet rubbing test, the testing square was thoroughly wet in distilled water. The rest of the procedure was the same as the dry test. The staining on the white testing cloth was assessed according to grey scale: 1-poor, 2-fair, 3-moderate, 4-good, and 5-excellent.

Fastness to sublimation

Sublimation fastness was measured with an iron tester (Yasuda no. 138). The samples were prepared by stitching pieces of dyed polyester fabric between two pieces of undyed polyester, all of equal diameter, and then treated at 180 and 210 °C 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, and 5-excellent.

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%, and 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, and 8-very good.

Color assessment

Table 1 reports the color parameters of the dyed fabrics assessed by tristimulus colorimetry. The color parameters of the dyed fabrics were determined using a SPECTRO multichannel photodetector (model MCPD1110A), equipped with a D65 source and barium sulfate as a standard blank. The values of the chromaticity coordinates, luminance factor, and the position of the color in the CIE-LAB color solid are reported.

In vitro antimicrobial activity

The tested compounds were evaluated by the agar diffusion technique [25] using a 2 mg/cm³ solution in DMSO. The test organisms were *B. thuringiensis* as Gram-positive bacteria and *E. coli* as Gram-negative bacteria. DMSO was used as a control for each organism. Ampicillin and chloramphenicol in DMSO were used as reference drugs.

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