Research Article

Thioxopyrimidine in Heterocyclic Synthesis III: Synthesis and Properties of Some Novel Heterocyclic Chalcone Derivatives Containing a Thieno[2,3-*d*]pyrimidine-Based Chromophore

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Cyclization of 4-methyl-2-phenyl-6-thioxo-1,6-dihydropyrimidine-5-carbonitrile **1** with chloroacetone in DMF in the presence of excess potassium carbonate anhydrous gave the 1-(5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidin-6-yl)ethanone **3**, which can react with 2,5-dimethoxytetrahydrofuran in glacial acetic acid producing the 1-[4-methyl-2-phenyl-5-(1*H*-pyrrol-1-yl)thieno[2,3-*d*]pyrimidin-6-yl]ethanone **4**. On the other hand, a series of novel 3-aryl-1-[4-methyl-2-phenyl-5-(1*H*-pyrrol-1-yl)-thieno[2,3-*d*]pyrimidin-6-yl]prop-2-en-1-one chalcone dyes **6a–n** were obtained by the condensation reaction of 1-[4-methyl-2-phenyl-5-(1*H*-pyrrol-1-yl)thieno[2,3-*d*]pyrimidin-6-yl]ethanone **4** with appropriate aldehydes. The structures of chalcone dyes were characterized by IR, ¹H NMR, mass, elemental analysis, and UV-Vis spectroscopy. The dyes were applied to polyester fibers for creating hues ranging from greenish-yellow to orange; their spectral characteristics, substituent effect in DMF solution, fastness properties, and colorimetric assessment are also discussed.

1. Introduction

The considerable biological and medicinal activity caused by fused thienopyrimidines has stimulated much research in this field [1–5]. Moreover, several series of heterocyclic compounds possessing a bridgehead pyrrolic moiety play a vital role in many biological activities [6–10]. Likewise, compounds with a chalcone-based structure have showed an array of pharmacological activities [11–16]. However, chalcones, the bichromophoric molecules separated by vinyl chains and the carbonyl group, are found being effective photosensitive materials and exhibit promising nonlinear optical properties [17]. On the other hand, molecular two-photon absorption (TPA) has attracted a lot of interest recently for its applications in the field of both biological imaging and materials science; TPA materials have recently received considerable attention [18–20]. A number of organic molecules have been studied for TPA activity [21–24]. Among these TPA systems, the heterocycle-based chromophores are particularly interesting due to their easily

polarizable heteroaromatic rings which can help to improve their degree of intramolecular charge transfer (ICT) [25–27]. Recently the synthesis and characterization of chromophores have been reported in which the donor moiety is represented by a π -excessive five-membered heterocycle (pyrrole or thiophene) and the acceptor group is a deficient heterocyclic azine ring (pyridine, pyrazine, pyrimidine, and pyridazine), which exhibit solvatochromic, electrochromic, photochromic, fluorescent, and nonlinear optical properties [28, 29]. Further developments involve the stretch of the charge transfer and the length of the π -bridge, such as multibranch octupoles or dendrimers [30].

Beyond these very important applications in biological chemistry, the chalcones are also found being used in the production of nematic liquid crystals [31], photosensitive polymers [32], antioxidants [33, 34], and as dyes [35, 36]. Although a number of papers concerning the synthesis of chalcone compounds have been published, those containing a new heterocyclic system of thieno[2,3-*d*]pyrimidine-based chromophores and application have not yet been

reported. Therefore, based on our previous works [37–39], we aim to report herein the preparation of a series of chalcone derivatives containing a thieno[2,3-*d*]-pyrimidine-based chromophore, and there was application to polyester fibers as disperse dyes. The spectral characteristics, dyeing properties, and colorimetric assessment of the dyes are also discussed.

2. Experimental

2.1. General. All melting points are uncorrected and in °C. IR spectra were recorded on a JASCO FTIR-3 spectrometer (KBr); ¹H NMR spectra were obtained on a Bruker AM-300 WB FI-NMR spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Electron impact mass spectra were obtained at 70 eV using a Finnigan Mat TSQ-46C spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 elemental Analyzer. Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in DMF at a concentration of 2×10^{-5} mol L⁻¹. Aldehydes **5a–n** were purchased from Aldrich and were used without further purification.

2.2. Synthesis of 1-(5-Amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidin-6-yl)ethanone (3). To a solution of 4-methyl-2-phenyl-6-thioxo-1,6-dihydropyrimidine-5-carbo-nitrile **1** (2.27 g, 0.01 mol) in DMF (50 mL), potassium carbonate anhydrous (2.76 g, 0.02 mol) and chloroacetone **2** (0.93 g, 0.01 mol) were added. The reaction mixture was stirred at room temperature for 4 h and then diluted with cold water (50 mL). The resulting solid product was collected by filtration, washed with water, and recrystallized from ethyl acetate/ethanol to give 2.66 g of yellow needles (94% yield), m.p. 210°C; IR: ν 3424, 3295 (NH₂), 1663 (C=O) cm⁻¹; ¹H NMR (CDCl₃): δ 2.47 (3H, s, COCH₃), 3.07 (3H, s, CH₃), 3.76 (2H, br, NH₂), 8.58–8.55, 7.60–7.55 (5H, m, phenyl-H); MS: 283 (M⁺, 100), 268 (95), 240 (20), 212 (2), 165 (5), 160 (10), 137 (34), 110 (18), 77 (9). Anal. Calcd. for C₁₅H₁₃N₃OS: C, 63.60; H, 4.59; N, 14.84. Found: C, 63.63; H, 4.50; N, 14.77%.

2.3. Synthesis of 1-[4-Methyl-2-phenyl-5-(1H-pyrrol-1-yl)thieno[2,3-*d*]pyrimidin-6-yl]ethanone (4). A mixture of 1-(5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidin-6-yl)ethanone **3** (2.83 g, 0.01 mol), 2,5-dimethoxytetrahydrofuran (1.26 g, 0.01 mol), in glacial acetic acid (20 mL) was refluxed for 12 h. After cooling, the resulting solid product was collected by filtration, washed with water, and the crude product recrystallized from ethanol/glacial acetic acid to give 2.96 g of gray white needles (89% yield), m.p. 204°C; IR: ν 1660 (C=O) cm⁻¹; ¹H NMR (CDCl₃): δ 2.09 (3H, s, COCH₃), 2.20 (3H, s, CH₃), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, t, 2,5-H of pyrrolyl), 8.56–8.54, 7.51–7.49 (5H, m, phenyl-H); MS: 333 (M⁺, 100), 318 (35), 290 (36), 277 (4), 223 (4), 185 (8), 166 (10), 160 (14), 116 (10), 103 (20), 77 (19), 51 (5). Anal. Calcd. for C₁₉H₁₅N₃OS: C, 68.46; H, 4.50; N, 12.61. Found: C, 68.33; H, 4.52; N, 12.59%.

TABLE 1: Physical and analytical data of 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine derivatives **6a–n**.

Dye	M.P. (°C) ^a	Yield (%)	Molecular formula	Elemental analysis (%)		
				Calcd/Found		
				C	H	N
6a	184	88	C ₂₆ H ₁₈ ClN ₃ OS	68.49	3.95	9.22
				68.55	4.02	9.33
6b	282	96	C ₂₈ H ₂₄ N ₄ OS	72.41	5.17	12.06
				72.58	5.21	12.12
6c	170	96	C ₂₇ H ₂₁ N ₃ OS	74.48	4.82	9.65
				74.44	4.92	9.55
6d	262	95	C ₂₇ H ₂₁ N ₃ O ₂ S	71.84	4.65	9.31
				71.80	4.71	9.45
6e	230	93	C ₃₀ H ₂₈ N ₄ OS	73.17	5.69	11.38
				73.22	5.74	11.24
6f	148	95	C ₃₂ H ₂₃ N ₃ OS	77.26	4.62	8.45
				77.23	4.77	8.56
6g	130	92	C ₂₄ H ₁₇ N ₃ O ₂ S	70.07	4.13	10.21
				70.15	4.22	10.36
6h	262	98	C ₂₄ H ₁₇ N ₃ OS ₂	67.44	3.98	9.83
				67.39	4.06	9.89
6i	278	95	C ₃₆ H ₂₃ N ₃ OS	79.26	4.22	7.70
				79.58	4.56	7.98
6j	178	98	C ₃₄ H ₂₆ N ₄ OS	75.83	4.83	10.40
				75.88	4.73	10.33
6k	152	93	C ₂₉ H ₂₅ N ₃ OS	75.16	5.40	9.07
				75.18	5.42	9.24
6l	210	84	C ₂₈ H ₂₂ N ₄ O ₂ S	70.29	4.60	11.71
				70.32	4.56	11.55
6m	228	90	C ₃₄ H ₂₃ N ₃ OS	78.31	4.41	8.06
				78.29	7.48	7.97
6n	286	94	C ₃₈ H ₂₈ N ₄ OS	77.55	4.76	9.52
				77.68	4.82	9.52

^a Recrystallization from DMF/ethanol.

2.4. Synthesis of 3-Aryl-1-[4-methyl-2-phenyl-5(1H-pyrrol-1-yl)thieno[2,3-*d*]pyrimidin-6-yl]prop-2-en-1-ones (6a–n) General Procedure. A mixture of compound **4** (0.33 g, 1.0 mmol), appropriate aldehydes **5a–n** (1.0 mmol) and NaOH (2.2 mmol) in absolute ethanol (10 mL) was stirred at room temperature for 24 h. The mixture was stirred at room temperature for 24 h. The mixture was acidified with dilute acetic acid, and the precipitated product was collected by filtration, washed with water, and the crude product recrystallized from THF/ethanol. The physical constants and spectral data of compounds **6a–n** are recorded in Tables 1 and 2.

2.5. Dyeing Procedure [40]. Polyester fabrics were dyed in a laboratory dyeing machine at a liquor ratio of 30 : 1. Dye bath

TABLE 2: Spectra data of 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidine derivatives **6a-n**.

Dye	MS (m/e M ⁺)	IR (KBr) ν (cm ⁻¹)	¹ H-NMR ^a (CF ₃ COOD) δ (ppm)
6a	455.5	1667 (C=O)	2.20 (3H, s, CH ₃), 5.80 (1H, d, <i>J</i> = 3.1 Hz, COCH=), 6.62 (2H, m, 3,4-H of pyrrolyl), 6.87 (2H, m, 2,5-H of pyrrolyl), 6.75 (2H, d, <i>J</i> = 1.00 Hz, 3,5-H of phenyl), 7.33 (2H, d, <i>J</i> = 1.00 Hz, 2,6-H of phenyl), 7.82 (1H, d, <i>J</i> = 3.1 Hz, =CH-), 8.57–8.55, 7.55–7.21 (5H, m, phenyl-H)
6b	464	1628 (C=O)	2.27 (3H, s, CH ₃), 3.06 (6H, s, N(CH ₃) ₂), 5.70 (1H, d, <i>J</i> = 3.1 Hz, COCH=), 6.59–6.50 (2H, m, 3,4-H of pyrrolyl), 6.98–6.87 (2H, m, 2,5-H of pyrrolyl), 6.70 (2H, d, <i>J</i> = 1.0 Hz, 3,5-H of phenyl), 7.25 (2H, d, <i>J</i> = 1.5 Hz, 2,6-H of phenyl), 7.75 (1H, d, <i>J</i> = 3.1 Hz, =CH-), 8.57–8.54, 7.51–7.50 (5H, m, phenyl-H).
6c	435	1663 (C=O)	2.27 (3H, s, CH ₃), 2.39 (3H, s, CH ₃), 6.02 (1H, d, <i>J</i> = 3.0 Hz, COCH=), 6.61–6.51 (2H, m, 3,4-H of pyrrolyl), 7.09–6.87 (2H, m, 2,5-H of pyrrolyl), 7.79 (1H, d, <i>J</i> = 3.0 Hz, =CH-), 8.59–8.58, 7.81–7.33 (9H, m, phenyl-H).
6d	451	1668 (C=O)	2.33 (3H, s, CH ₃), 3.84 (3H, s, OCH ₃), 5.75 (1H, d, <i>J</i> = 3.1 Hz, COCH=), 6.60 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, d, <i>J</i> = 1.0 Hz, 3,5-H of phenyl), 6.99 (2H, t, 2,5-H of pyrrolyl), 7.28 (2H, d, <i>J</i> = 1.0 Hz, 2,6-H of phenyl), 7.76 (1H, d, <i>J</i> = 3.0 Hz, =CH-), 8.59–8.55, 7.52–7.51 (5H, m, phenyl-H).
6e	492	1628 (C=O)	1.21 (6H, t, <i>J</i> = 1.4 Hz, CH ₃), 2.27 (3H, s, CH ₃), 3.41 (4H, q, <i>J</i> = 1.4 Hz, CH ₂), 5.68 (1H, d, <i>J</i> = 3.1 Hz, COCH=), 6.59–6.49 (4H, m, 3,4-H of pyrrolyl and 3,5-H of phenyl), 6.98–6.87 (2H, m, 2,5-H of pyrrolyl), 7.24 (2H, d, <i>J</i> = 1.0 Hz, 2,6-H of phenyl), 7.74 (1H, d, <i>J</i> = 3.0 Hz, =CH-), 8.56–8.53, 7.50–7.49 (5H, m, phenyl-H).
6f	497	1667 (C=O)	2.18 (3H, s, CH ₃), 5.75 (1H, d, <i>J</i> = 3.0 Hz, COCH=), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.86 (2H, t, 2,5-H of pyrrolyl), 8.65–8.54, 7.63–7.38 (15H, m, =CH- and phenyl-H).
6g	411	1667 (C=O)	2.28 (3H, s, CH ₃), 5.88 (1H, d, <i>J</i> = 3.1 Hz, COCH=), 6.59–6.48 (3H, m, 3,4-H of pyrrolyl and 4-H of furyl), 6.87 (2H, m, 2,5-H of pyrrolyl), 7.00 (1H, d, <i>J</i> = 2.0 Hz, 3-H of furyl), 8.15 (1H, d, <i>J</i> = 3.0 Hz, =CH-), 8.63–8.54, 7.58–7.48 (6H, m, 5-H of furyl and phenyl-H).
6h	427	1641 (C=O)	2.11 (3H, s, CH ₃), 5.47 (1H, d, <i>J</i> = 3.2 Hz, COCH=), 6.63–6.39 (3H, m, 3,4-H of pyrrolyl and 4-H of thienyl), 7.06–7.03 (2H, m, 2,5-H of pyrrolyl), 7.13 (1H, d, <i>J</i> = 1.0 Hz, 3-H of thienyl), 7.80 (1H, d, <i>J</i> = 3.0 Hz, =CH-), 8.48–8.45, 7.54–7.44 (6H, m, 5-H of thienyl and phenyl-H).
6i	545	1623 (C=O)	2.06 (3H, s, CH ₃), 5.79 (1H, d, <i>J</i> = 3.1 Hz, COCH=), 6.51 (2H, m, 3,4-H of pyrrolyl), 6.90 (2H, m, 2,5-H of pyrrolyl), 8.62–8.42, 8.32–8.05 (15H, m, =CH-, phenyl-H and pyrenyl-H).
6j	538	1633 (C=O)	1.77 (3H, t, <i>J</i> = 1.2 Hz, CH ₃), 2.52 (3H, s, CH ₃), 4.03 (2H, d, <i>J</i> = 1.0 Hz, CH ₂), 5.79 (1H, d, <i>J</i> = 3.0 Hz, COCH=), 6.51 (2H, m, 3,4-H of pyrrolyl), 6.90 (2H, m, 2,5-H of pyrrolyl), 8.72–7.61, (13H, m, =CH-, phenyl-H and carbazolyl-H).
6k	463	1643 (C=O)	2.10 (3H, s, CH ₃), 2.22 (6H, s, CH ₃), 2.28 (3H, s, CH ₃), 5.88 (1H, d, <i>J</i> = 4.0 Hz, COCH=), 6.51–6.45 (2H, m, 3,4-H of pyrrolyl), 6.88–6.84 (2H, m, 2,5-H of pyrrolyl), 7.39 (1H, d, <i>J</i> = 1.2 Hz, =CH-), 8.58–8.53, 7.54–7.51 (7H, m, phenyl-H).
6l	478	3324 (NH), 1622 (C=O)	2.06 (3H, s, CH ₃), 2.16 (3H, s, COCH ₃), 5.78 (1H, d, <i>J</i> = 3.0 Hz, COCH=), 6.49 (2H, m, 3,4-H of pyrrolyl), 6.97 (2H, m, 2,5-H of pyrrolyl), 6.87 (2H, d, <i>J</i> = 1.00 Hz, 3,5-H of phenyl), 7.57 (1H, d, <i>J</i> = 1.5 Hz, =CH-), 8.50–8.29, 7.47–7.41 (7H, m, phenyl-H), 8.29 (1H, br, NH).
6m	521	1679 (C=O)	2.22 (3H, s, CH ₃), 6.13 (1H, d, <i>J</i> = 3.0 Hz, COCH=), 6.24 (2H, m, 3,4-H of pyrrolyl), 6.91 (2H, m, 2,5-H of pyrrolyl), 8.93–7.99, 7.54–7.26 (15H, m, =CH-, phenyl-H and anthracenyl-H).
6n	588	1631 (C=O)	2.30 (3H, s, CH ₃), 5.71 (1H, d, <i>J</i> = 3.0 Hz, COCH=), 6.55 (2H, t, 3,4-H of pyrrolyl), 6.98–6.94 (4H, m, 3,5-H of phenyl and 2,5-H of pyrrolyl), 7.74 (1H, d, <i>J</i> = 3.0 Hz, =CH-), 8.59–8.57, 7.53–7.13 (17H, m, phenyl-H).

^a s: Singlet; d: doublet; t: triplet; m: multiplet; br: broad.

(60 mL) was prepared with formulated dye and a dispersing agent (Diwatec 40, 0.5 g L⁻¹) and adjusted to pH 4.0. The polyester fabric (2.0 g) was immersed in the dye bath and dyed for 60 min at 130°C. After dyeing, the dyed fabric was reduction cleared (Na₂S₂O₄ 2.0 g L⁻¹, NaOH 2.0 g L⁻¹, soaping agent 2.0 g L⁻¹) for 20 min at 75°C.

2.6. Fastness Test. The light fastness was determined using standard procedures [41]. For sublimation fastness determinations, the dyed polyester fibers were stitched between two pieces of undyed polyester fibers (stain cloth) and treated at 200°C for 1 min. Any staining on the undyed piece, change in tone, or loss in depth was assessed on 1 (poor) to 5 (very good) rating.

2.7. Colorimetric Analysis. The color parameters of the dyed polyester fabrics were measured using the Applied Color System, CS-5 chroma-sensor, model 502 using D₆₅ source and ultraviolet radiation [42]. Each fabric sample was folded twice so as to realize a total of four thicknesses of fabric. The assessment of color-dyed fabrics was made in terms of tristimulus colorimetry [43]. The CIE attributes of lightness (*L*^{*}), chroma (*C*^{*}), and hue (*a*^{*} value represents the degree of redness (positive) and greenness (negative) and *b*^{*} represents the degree of yellowness (positive) and blueness (negative)) were calculated in the present work.

3. Results and Discussion

3.1. Synthesis and Spectral Characteristics. All relevant reactions are depicted in Schemes 1 and 2. 4-Methyl-2-phenyl-6-thioxo-1,6-dihydropyrimidine-5-carbonitrile **1**, which is required as a starting material, was prepared in our previously reported [44]. Cyclization of thioxopyrimidine **1** with chloroacetone **2** in DMF in the presence of excess anhydrous potassium carbonate at room temperature gave the 1-(5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidin-6-yl)ethanone **3** in good yields (Scheme 1). The possible mechanism for formation of compound **3** can be explained by the reaction pathway depicted in Scheme 1. The IR spectrum of the compound **3** indicated the absence of the C≡N and C=S groups, and the amino group appears at 3424–3259 cm⁻¹ in the form of two bands due to intramolecular association between the 5-NH₂ and 6-COCH₃ groups of compound **3** and the characteristic absorption band at 1663 cm⁻¹ for the carbonyl group (C=O). In addition, the ¹H NMR spectra (CDCl₃) of compound **3** showing a singlet at δ 2.47 (3H, s) assigned for the acetyl group, a broad singlet at 3.76 (2H, br) assigned to the NH₂ protons, and a multiplet at δ 8.58–7.55 (5H, m) assigned to the phenyl protons were also confirmed by the mass spectra *m/z* 283 (M⁺, 100).

Moreover, treatment of compound **3** with 2,5-dimethoxytetrahydrofuran in glacial acetic acid produced the 1-[4-methyl-2-phenyl-5-(1*H*-pyrrol-1-yl)thieno[2,3-*d*]pyrimidin-6-yl]ethanone **4** (Scheme 1). The IR spectrum of the compound **4** indicates the absence of the NH₂ group. The ¹H NMR spectra (CDCl₃) of the compound **4** show a

singlet at δ 2.09 (3H, s) assigned for the acetyl group and two triplets at δ 6.50 (2H, t) and 6.87 (2H, t), which were readily assigned to the hydrogen attached at C₃, C₄ and C₂, and C₅ of the pyrrolyl ring, respectively. On the other hand, the 3-aryl-1-[4-methyl-2-phenyl-5-(1*H*-pyrrol-1-yl)thieno[2,3-*d*]pyrimidin-6-yl]prop-2-en-1-one chalcone dyes **6a–n** were obtained in good yields (84–98%) based on Claisen-Schmidt condensation of compound **4** with appropriate aldehydes **5a–n** (Scheme 2). The formation of compounds **6a–n** can be explained by the reaction pathway depicted in Scheme 2. The mechanism [44] involves base (OH⁻) removes a C–H proton of CH₃CO group in compound **4** to give carbanion **4'**, which then adds to C=O group in aldehydes **5**, followed then undergoes condensation via dehydration affording the final products **6a–n**. The structures of dyes **6a–n** were established by examining spectral data and elemental analysis. The IR spectrum of dyes **6a–n** indicates the characteristic absorption bands at 1679–1622 cm⁻¹ for the C=O group. Physical and spectral data of dyes **6a–n** are given in Tables 1 and 2.

3.2. Absorption Spectral Characteristics. The absorption maxima (λ_{max}) of the dyes **6a–n** were measured in DMF solution and are listed in Table 3. The absorption maxima of the dyes **6a–n** ranged from 412 to 488 nm, with dye **6e** showing the highest λ_{max} (488 nm) and **6a** the lowest (412 nm). Color shifts are in accord with variations resultant from changes in substituents in these dyes. As seen from Table 3, structural modification occurs only in one terminal moiety, where a *p*-chlorophenyl donor **6a** was replaced by a dialkyl(aryl)aminophenyl or heteroaryl or polycyclic groups. Such a modification could be expected to result in notable changes in the π-conjugated and red shifts in the absorption spectra. The λ_{max} of dyes **6a–n** is related to intramolecular charge transfer (ICT) chromophoric system in which these molecules consist of a typical A-π-D structure, where 6-carbonyl-pyrrolythieno[2,3-*d*]pyrimidinyl, vinyl, and substituent moieties (R) are employed as acceptor (A), π-conjugated center (π), and donor (D) moieties, respectively. The absorption maxima are mainly dominated by the nature of the excited state π-electron system. As well known, a strong electron donor could help to stabilize the charge-separated excited state of the molecule; the red-shift could be explained by the electron-donating strength of donor group [35, 46].

Compound **6a**, as a standard, absorbed at 412 nm and substituent effects on the absorption maxima were evaluated compared with this value. As is apparent in Table 3, introduction of electron-donating substituents into the 6-carbonyl-pyrroly-thieno[2,3-*d*]pyrimidinyl-based chromophore produces a significant bathochromic shifts of the absorption maxima. The differences of these values are shown by Δλ_{max}. As a result, the dyes **6b–n** were bathochromic shift of 11–76 nm. It can be seen from Table 3 that dyes **6b**, **6e**, **6l**, and **6n** selected in this case produced bathochromic shifts of 41 to 76 nm caused by introduction of the stronger electron-donating substituents (dialkyl(aryl)aminophenyl) into 6-carbonyl-pyrrolythieno[2,3-*d*]pyrimidinyl-based chromophore at which there is an electron density decrease

SCHEME 1: Synthesis of compound 4.

that should produce a bathochromic shift of $\lambda_{\max}$ [46]. In general, with respect to the substituents R of dyes **6b**, **6e**, **6l**, and **6n**, the dyes were bathochromically shifted in the following order: diethylaminophenyl (**6e**) ($\Delta\lambda_{\max}$ 76 nm)>diphenylaminophenyl (**6n**) ($\Delta\lambda_{\max}$ 58 nm)>dimethylaminophenyl (**6b**) ($\Delta\lambda_{\max}$ 43 nm)>4-acetamidophenyl (**6l**) ($\Delta\lambda_{\max}$ 41 nm). Furthermore, the spectroscopic data also demonstrate that the dye **6e** ($\lambda_{\max}$ 488 nm) containing the diethylaminophenyl group showed a largest bathochromic shift of 76 nm.

On the other hand, $\lambda_{\max}$ value in the case of selected dyes **6c**, **6f**, **6i**, **6j**, **6k**, and **6m** indicates that replacement of the p-chlorophenyl group of dye **6a** for appropriate heteroaryl or polycyclic substituents, such as tolyl (**6c**), biphenyl (**6f**), pyrenyl (**6i**), carbazolyl (**6j**), 2,4,6-trimethylphenyl (**6k**), and anthryl (**6m**), leads to a significant bathochromic shift of 11 to 69 nm. The differences of these values are shown by $\Delta\lambda_{\max}$. For instance, dye **6a** was absorbed at 412 nm, with increasing donor ability from the p-chlorophenyl (**6a**) to the carbazolyl (**6j**), pyrenyl (**6i**), and anthryl (**6m**); their $\Delta\lambda_{\max}$ values show large bathochromic shifts to 442 nm ($\Delta\lambda_{\max}$ = 30 nm), 478 nm ($\Delta\lambda_{\max}$ = 66 nm), and 481 nm ($\Delta\lambda_{\max}$ = 69 nm), respectively. In general, with respect to the substituents R of dyes **6c**, **6f**, **6i**, **6j**, **6k**, and **6m**, the dyes were bathochromically shifted in the following order: anthryl (**6m**) ($\Delta\lambda_{\max}$ 69 nm)>pyrenyl (**6i**) ($\Delta\lambda_{\max}$ 66 nm)>biphenyl (**6f**) ($\Delta\lambda_{\max}$ 44 nm)>carbazolyl (**6j**) ($\Delta\lambda_{\max}$ 30 nm)>2,4,6-trimethylphenyl (**6k**) ($\Delta\lambda_{\max}$ 28 nm)>tolyl (**6c**) ($\Delta\lambda_{\max}$

11 nm). Moreover, the spectroscopic data also demonstrate that the dye **6g** ($\lambda_{\max}$ 442 nm) containing the furyl moiety shows a bathochromic shift of 18 nm in comparison with the dye **6h** ($\lambda_{\max}$ 424 nm) containing the thienyl moiety.

In brief, dyes derived from dialkyl(aryl)aminophenyl substituents exhibited significantly larger bathochromic shift compared with those derived from heteroaryl or polycyclic substituents. Furthermore, it is well known that molar extinction coefficients ϵ values reflect the molecular planarity and enlargement of π -conjugation. The dyes **6c**, **6f**, **6k**, and **6m** have bigger ϵ values than those of other dyes which indicates that dyes **6c**, **6f**, **6k**, and **6m** have much more planar and rigid π -conjugation system than that of other dyes [47].

3.3. Dyeing and Fastness Properties. For imparting greenish-yellow to orange hues, the dyes **6a–n** were applied to polyester fiber at 1% shade by high-temperature-pressure techniques. The fastness properties of the dyes are shown in Table 3. Table 3 shows that the light fastness of these dyes varied from 1–5; thus the dyes **6b**, **6e**, **6g**, **6j**, **6k**, and **6l** had poor light fastness (1–2), dyes **6c**, **6d**, **6f**, **6h**, **6i**, and **6m** had fair light fastness (3–4), and dyes **6a** and **6n** had good light fastness (4–5). In general, the dyes in the range of 3–5 show good sublimation fastness properties on polyester fibers.

3.4. Colorimetric Assessment. Three important attributes of color that must be considered in the development of new colorants are lightness, chroma, and hue. These attributes can

SCHEME 2: Synthesis of chalcone dyes **6(a-n)**.

be determined by colorimetric assessment using the prototype dye. The CIE attributes of lightness (L^*), chroma (C^*), and hue (a^* = redness/greenness; b^* = yellowness/blueness) were calculated in the present work. The values of the CIE coordinate (L^* , a^* , b^* , h° , and C^*) are listed in Table 4. According to Richter [48] and McLaren et al. [49] the position of the color is distributed in the red-green area with hue angle h° 33.07–116.83° and radial chroma C^* of length 8.35–48.08. Figure 1 shows a graph of CIE coordinates a^* versus b^* for selected dyes **6b**, **6e**, **6l**, and **6n** (an increasing a^* value represents an increase in redness, while a decrease in a^* represents a green hue shift). Dyes **6l** and **6n** provided a reference point for the color attributes of each dye, since **6l** is

a yellow and **6n** is a strong orange. The dye based on dimethylaminophenyl (**6b**) was yellow-orange, and thus the a^* b^* graph shows the dye to be bathochromic compared with **6l** and hypsochromic relative to **6n**. Apart from **6e** and **6n**, dyes displayed similar hues both to each other and to **6l**. Hence, the presence of stronger electron-donating substituents in the 6-carbonyl-pyrrolythieno[2,3-*d*]pyrimidinyl-based chromophore linkage produced the desired colorimetric effect.

Furthermore, Figures 2 and 3 show a graph of CIE C^* versus L^* for selected dyes (**6b**, **6e**, **6l** and **6n**) and (**6a**, **6c**, **6d**, **6f–6k**, and **6m**), respectively. In general, dyes derived from dialkyl(aryl)aminophenyl substituents exhibited significantly higher chroma compared with those derived from

TABLE 3: Absorption spectra and dyeing properties of 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidine derivatives **6a–n**.

Dye	R	Colour on dyed polyester fibers	$\lambda_{\max}$ (DMF)(nm)	$\epsilon \times 10^4$ (mol ⁻¹ cm ⁻¹)	$\Delta\lambda_{\max}$	Light fastness	Sublimation fastness
6a		Light yellow	412	6.02	—	5	3-4
6b		Orange	455	1.83	43	1-2	4
6c		Greenish yellow	423	8.43	11	3-4	3-4
6d		Yellow	424	6.24	12	3-4	3-4
6e		Orange	488	3.81	76	2	3
6f		Yellow	456	9.34	44	3-4	5
6g		Yellow	442	6.64	30	2-3	4
6h		Yellow	424	6.23	12	3	4-5
6i		Yellow	478	3.04	66	3-4	4-5
6j		Light yellow	442	4.39	30	1	5
6k		Greenish yellow	440	8.68	28	2	3-4
6l		Yellow	453	1.13	41	2	4-5
6m		Orange yellow	481	7.17	69	3	5
6n		Orange	470	4.09	58	4-5	4-5

TABLE 4: CIE of dyes **6a–n** on polyester.

Dye	L^*	a^*	b^*	C^*	h°	K/S
6a	88.40	0.09	9.52	9.52	90.56	0.1789
6b	91.32	17.34	37.98	41.76	65.46	0.9125
6c	84.29	−3.77	7.45	8.35	116.83	0.3417
6d	91.06	−6.12	21.90	22.74	105.60	0.4236
6e	85.84	33.35	34.63	25.55	46.06	1.3319
6f	89.61	−0.79	15.38	15.40	92.96	0.2368
6g	73.24	6.04	15.97	17.07	69.27	0.7793
6h	88.41	−3.80	24.22	24.52	98.92	0.5565
6i	89.52	−0.10	11.27	11.27	90.50	0.3050
6j	90.60	−6.69	33.96	34.61	101.14	0.8942
6k	82.53	−2.94	12.51	12.85	103.22	0.6437
6l	85.06	5.34	24.99	48.08	46.08	0.4600
6m	83.41	9.27	20.99	22.95	66.18	0.3820
6n	76.37	35.23	22.94	42.04	33.07	0.5334

FIGURE 1: Graph of CIE a^* versus b^* for selected dyes. FIGURE 2: Graph of CIE C^* versus L^* for selected dyes.

heteroaryl or polychic substituents. Figure 2 shows that the dyes **6b**, **6e**, and **6l** were lighter than **6n**. Similar results are observed in Figure 3; the lightness of **6a**, **6c**, **6d**, **6f**, **6h–k**, and **6m** were all high except for dye **6g**.

On the other hand, Figure 4 shows a graph of CIE coordinates a^* versus b^* for selected dyes **6a**, **6c**, **6d**, **6f–6k** and **6m**. As the b^* scale represents yellowness (increasing b^* value) versus blueness (decreasing b^* value), it is evident that most of the new dyes were significantly yellower than **6c**. The dye **6f** based on biphenyl possessed approximately the same yellowness but was redder than dye **6j**. However, the dyes **6c**, **6d**, **6h**, and **6k** were green hue shift relative to the dye **6f**, although not as green as **6j**, and were similar in hue to **6d**. Also, the dyes based on p-chlorophenyl (**6a**) and tolyl (**6c**) were bluer than biphenyl (**6f**) and 2,4,6-trimethylphenyl (**6k**). In the case of **6a** and **6c**, the hypsochromic shift due to the presence of weak electron-donating substituents in the 6-carbonyl-pyrrolythieno[2,3-*d*]pyrimidinyl-based chromophore linkage is significant. In addition, dyes based on

furyl (**6g**) and anthryl (**6m**) were bathochromic relative to when p-chlorophenyl (**6a**) was employed.

4. Conclusions

Fourteen novel heterocyclic chalcone derivatives containing a thieno-[2,3-*d*]pyrimidine-based chromophore were obtained from thioxopyrimidine **1**. The chalcone derivatives were applied to polyester fibers as disperse dyes for creating hues ranging from greenish-yellow to orange. The substituent effect in DMF solution was also discussed. The results indicate that the novel chalcone dyes derived from dialkyl(aryl)aminophenyl substituents exhibited significantly larger bathochromic shift compared with those derived from heteroaryl or polycyclic substituents. On the other hand, color shifts are in accord with variations resultant from changes in substituents in these dyes. In general, the presence of dialkyl(aryl)aminophenyl substituents in the thieno[2,3-*d*]pyrimidinyl-based chromophore linkage produced the red hue shift, while the heteroaryl or polychic

FIGURE 3: Graph of CIE C^* versus L^* for selected dyes. FIGURE 4: Graph of CIE a^* versus b^* for selected dyes.

substituents produced the green hue shift. In addition, these dyes showed good sublimation fastness and poor- to good-light fastness on polyester fibers.

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