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The synthesis, structure and spectroscopic properties of novel oxazolone-, pyrazolone- and pyrazoline-containing heterocycle chromophores

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ABSTRACT

A series of novel heterocycle-based chromophores containing oxazolone, pyrazolone or pyrazoline moieties were synthesized under microwave irradiation and characterized using elemental analysis, IR, ^{1}H NMR spectroscopy and mass spectrometry. The crystal structures of two of the dyes were found, using single crystal X-ray crystallography, to be monoclinic, space group $P2_1/c$ types; the two molecules adopted a *Z* configuration about the central olefinic bond. The heterocyclic chromophores were fluorescent, with some examples emitting blue light (410–460 nm) whilst others emitted green light (529 nm). The absorption maxima of the chromophores were found to vary from 349 to 463 nm depending on the extent of conjugation.

1. Introduction

Nitrogen heterocycles are of special interest because they constitute an important class of natural and nonnatural products, many of which exhibit useful biological activities and unique electrical and optical properties [1–5]. Oxazolone, pyrazolone and pyrazoline derivatives are in general well-known five-membered nitrogen-containing heterocyclic compounds. Pyrazolone derivatives play an important role as substructures of numerous pharmaceuticals, agrochemicals, dyes and pigments, as well as chelating and extracting agents [6]. Moreover, they are capable of prototropic tautomerism [7]. Furthermore, pyrazoline derivatives show stronger fluorescence, and have higher hole-transport efficiency and excellent emitting blueness property. Therefore, pyrazoline derivatives have widely been used as whitening or brightening reagents for synthetic fibers, as fluorescence probes in some elaborated chemosensors, as fluorescent chemosensors for recognition of transition metal ions, as hole-transport materials in the electrophotography and electroluminescence fields [8–10].

On the other hand, oxazolone derivatives are highly versatile intermediates used for the synthesis of several organic molecules, including amino acids, peptides, antimicrobial or antitumor compounds, immunomodulators, heterocyclic precursors for biosensors coupling, and photosensitive composition devices for proteins [11–13]. Also, it was ever reported that some of 4-(substitutedbenzylidene)-2-substituted-4*H*-oxazol-5-one compounds exhibit promising nonlinear optical properties in solid state and in solution [14,15]. For example, the second-order harmonic generation (SHG) values of 4-benzo-[1,3]dioxol-5-ylmethylene-2-phenyl-4*H*-oxazol-5-one and 4-(3,4,5-trimethoxy-benzylidene)-2-phenyl-4*H*-oxazol-5-one are 5.603 and 1.821, respectively, as compared with urea powder [14]. Also, we have reported previously the synthesis and crystal structures of some oxazolone and pyrazolone derivatives [16–19].

Due to the possible importance of these compounds and our interest in the development of heterocycle-based chromophores, in this study, we wish to report the synthesis of some new heterocycle-based chromophores based on oxazolone, pyrazolone or pyrazoline cores, including two oxazolone derivatives (**1a** and **1b**), four pyrazolone derivatives (**2a**–**2d**) and two pyrazoline derivatives (**3a** and **3b**), under microwave irradiation. Specially, we have focused on the coupling of two excellent molecular moieties, coumarin and pyrazoline. Our purpose is that it might be possible to develop new organic functional materials by satisfactory combination of coumarin and pyrazoline groups through appropriate molecular design and synthesis. Therefore, a new type of fluorescent dye, coumarin–pyrazoline hybrid (**3b**), has been synthesized by a combination of coumarin and benzothiazole

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through a pyrazoline unit in one molecule. At the same time, the preliminary spectroscopic properties and crystal structures are discussed. The synthetic pathway and the structures of target molecules are shown in Figs. 1–3.

2. Experimental

2.1. Chemicals and instrument

All melting points were determined with a WRS-1A melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were run on a Bruker AV-400 or DRX-500 NMR spectrometer and chemical shifts expressed as δ (ppm) values with TMS as internal standard. IR spectra were recorded in KBr on a Nicolet NEXUS 870 FT-IR spectrophotometer. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). Element analysis was taken with a Perkin–Elmer 240 analyzer. Mass spectra (MS) were measured on an API4000 or VG ZAB-HS mass spectrometer. Single crystal was characterized by Enraf-Nonius CAD-4 X-ray single crystal diffractometer. All the chemicals are commercially available and they were used without further purification.

2.2. Synthesis

2.2.1. General procedure for the synthesis of oxazolone derivatives *1a* and *1b*

A mixture of hippuric acid (2.2 mmol), appropriate aryl or heteroaryl aldehydes (2 mmol), anhydrous sodium acetate (3 mmol) in acetic anhydride (8 mL) was irradiated in a Galanz microwave oven for an optimized time and taken out for a few seconds and at the same time, the mixture was stirred carefully using a bar. The mixture was subjected to microwave irradiation for another optimized time and then taken out for stirring. The operation was repeated several times, and the reaction mixture was monitored by TLC. After the reaction was completed, the reaction mixture was cooled, diluted with ethanol (10 mL). The resulting mixture was left over night at room temperature. The solid thus obtained was filtered, dried and crystallized from ethanol to get title compound.

*2.2.1.1. 4-((6-Isopropyl-4-oxo-4*H*-1-benzopyran-3-yl)methylidene)-2-phenyl-1,3-oxazol-5(4*H*)-one (**1a**).* Yellow crystals, yield 49%; mp 218–221 °C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS) δ: 1.27 (d, J = 6.9 Hz, 6H), 3.02–3.16 (m, 1H), 7.41 (s, 1H), 7.65 (t, J = 7.5 Hz, 2H), 7.70–7.75 (m, 2H), 7.82 (d, J = 8.7 Hz, 1H), 7.99 (s, 1H), 8.21 (d, J = 7.5 Hz, 2H), 9.76 (s, 1H). IR (KBr) ν: 1792, 1767, 1649, 1613, 1602, 1567, 1480, 1457, 1326, 1299, 1188, 1154, 970, 887, 824, 782, 760, 700, 599 cm^{-1}. MS m/z: 360.4 (M + 1). Anal. calcd for $C_{22}H_{17}NO_4$: C 73.53, H 4.77, N 3.90; found: C 73.24, H 4.86, N 3.62.

*2.2.1.2. 4-(4-(Benzoxazol-2-yl)benzylidene)-2-phenyl-1,3-oxazol-5(4*H*)-one (**1b**).* Orange solid, yield 56%; mp 255–257 °C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS) δ: 7.46–7.51 (m, 3H), 7.68 (t, J = 7.4 Hz, 2H), 7.77 (t, J = 7.6 Hz, 1H), 7.86 (t, J = 8.9 Hz, 2H), 8.19 (d, J = 8.2 Hz, 2H), 8.35 (d, J = 8.3 Hz, 2H), 8.54 (d, J = 8.3 Hz, 2H). IR (KBr) ν: 1796, 1652, 1597, 1570, 1489, 1450, 1325, 1297, 1243, 1164, 1057, 983, 842, 763, 744, 694, 559 cm^{-1}. MS m/z: 367 (M + 1). Anal. calcd for $C_{23}H_{14}N_2O_3$: C 75.40, H 3.85, N 7.65; found: C 75.61, H 4.13, N 7.38.

2.2.2. General procedure for the synthesis of pyrazolone derivatives *2a–2d*

For the preparation of compounds **2a–2d**, 2 mmol of 3-methyl-1-phenyl-pyrazol-5-one, 2 mmol of appropriate aryl aldehydes and 20 mL of ethylene glycol were mixed together at ambient temperature. The mixture was irradiated in a microwave oven for an optimized time according to the above mentioned method. Then the reaction mixture was poured into water. The solid product was filtrated, dried and recrystallized from ethanol or ethyl acetate.

*2.2.2.1. 4-((6-Isopropyl-4-oxo-4*H*-1-benzopyran-3-yl)methylidene)-3-methyl-1-phenyl-pyrazol-5(4*H*)-one (**2a**).* Red solid, yield 43%; mp 182–184 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ: 1.35 (d, J = 7.0 Hz, 6H), 2.43 (s, 3H), 3.01–3.15 (m, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.65 (dd, J_1 = 8.5, J_2 = 2.0 Hz, 1H), 7.96 (d, J = 7.5 Hz, 2H), 8.06 (s, 1H), 8.16 (d, J = 2.0 Hz, 1H), 10.83 (s, 1H). IR (KBr) ν: 1688, 1645, 1627, 1612, 1597, 1537, 1500, 1477, 1364, 1322, 1289, 1227, 1145, 1112, 1001, 827, 806, 792, 753, 688, 664, 574 cm^{-1}. MS m/z: 373.4 (M + 1). Anal. calcd for $C_{23}H_{20}N_2O_3$: C 74.18, H 5.41, N 7.52; found: C 72.49, H 6.75, N 9.51.

*2.2.2.2. 4-(4-Hydroxy-3,5-dimethoxybenzylidene)-3-methyl-1-phenyl-pyrazol-5(4*H*)-one (**2b**).* Red crystals, yield 62%; mp 210–212 °C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS) δ: 2.33 (s, 3H), 3.87 (s, 6H), 7.19 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.9 Hz, 2H), 7.74 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 8.29 (s, 2H), 10.01 (s, 1H). IR (KBr) ν: 3336, 1656, 1614, 1595, 1558, 1508, 1461, 1431, 1356, 1310, 1271, 1216, 1142, 1114,

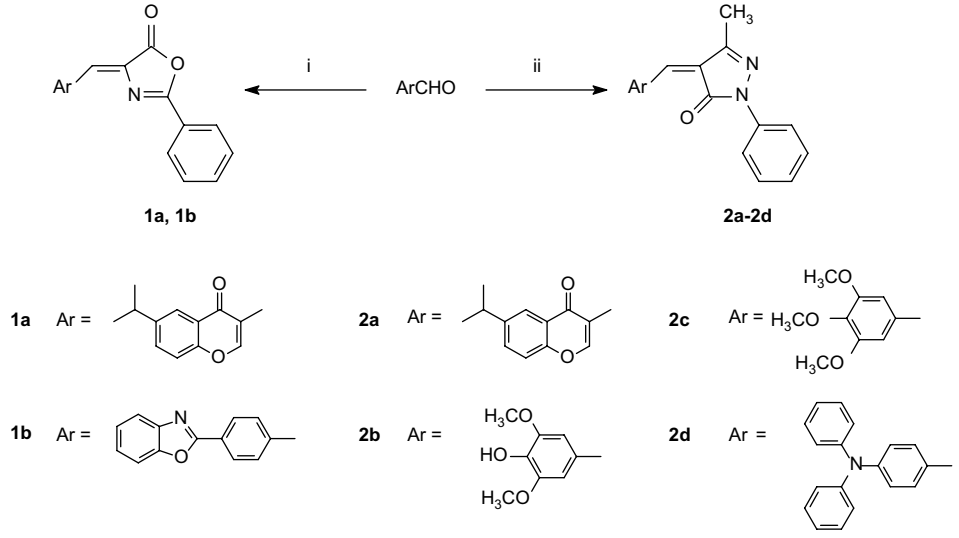

Fig. 1. Reagents and reaction conditions: (i) $PhCONHCH_2CO_2H$, NaOAc, Ac_2O, MW; (ii) 3-Methyl-1-phenyl-5-pyrazolone, MW.

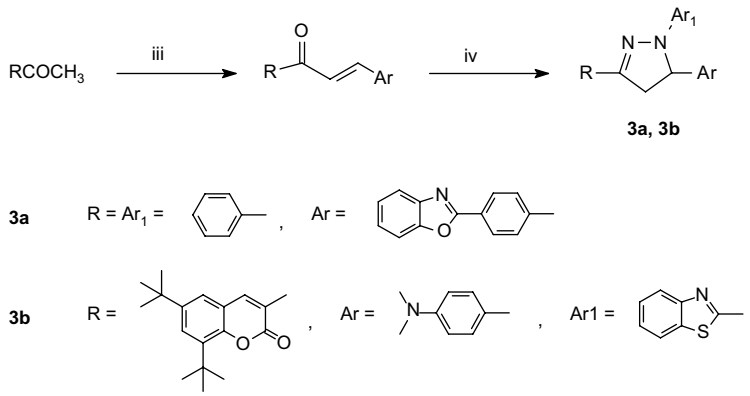

Fig. 2. Reagents and reaction conditions: (iii) ArCHO, piperidine, EtOH, reflux; (iv) Ar_1NHNH_2, Ethylene glycol, MW.

998, 872, 767, 699, 591 cm^{-1}. MS *m*/*z*: 339 (M + 1). Anal. calcd for $C_{19}H_{18}N_2O_4$: C 67.45, H 5.36, N 8.28; found: C 67.26, H 5.54, N 8.03.

*2.2.2.3. 3-Methyl-1-phenyl-4-(3,4,5-trimethoxy-benzylidene) pyrazol-5(4H)-one (**2c**).* Red solid, yield 67%; mp 143–145 °C. ^1H NMR (400 MHz, DMSO-d_6/TMS) δ: 2.34 (s, 3H), 3.81 (s, 3H), 3.88 (s, 6H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.80 (s, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 8.23 (s, 2H). IR (KBr) ν: 1672, 1609, 1597, 1563, 1499, 1456, 1298, 1254, 1128, 995, 931, 768, 753, 688, 587 cm^{-1}. MS *m*/*z*: 353.4 (M + 1). Anal. calcd for $C_{20}H_{20}N_2O_4$: C 68.17, H 5.72, N 7.95; found: C 68.33, H 5.87, N 8.15.

*2.2.2.4. 3-Methyl-1-phenyl-4-(4-N,N-diphenylaminobenzylidene) pyrazol-5(4H)-one (**2d**).* Red crystals, yield 64%; mp 179–181 °C. ^1H NMR (400 MHz, DMSO-d_6/TMS) δ: 2.31 (s, 3H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 1H), 7.24–7.48 (m, 12H), 7.65 (s, 1H), 7.91 (d,

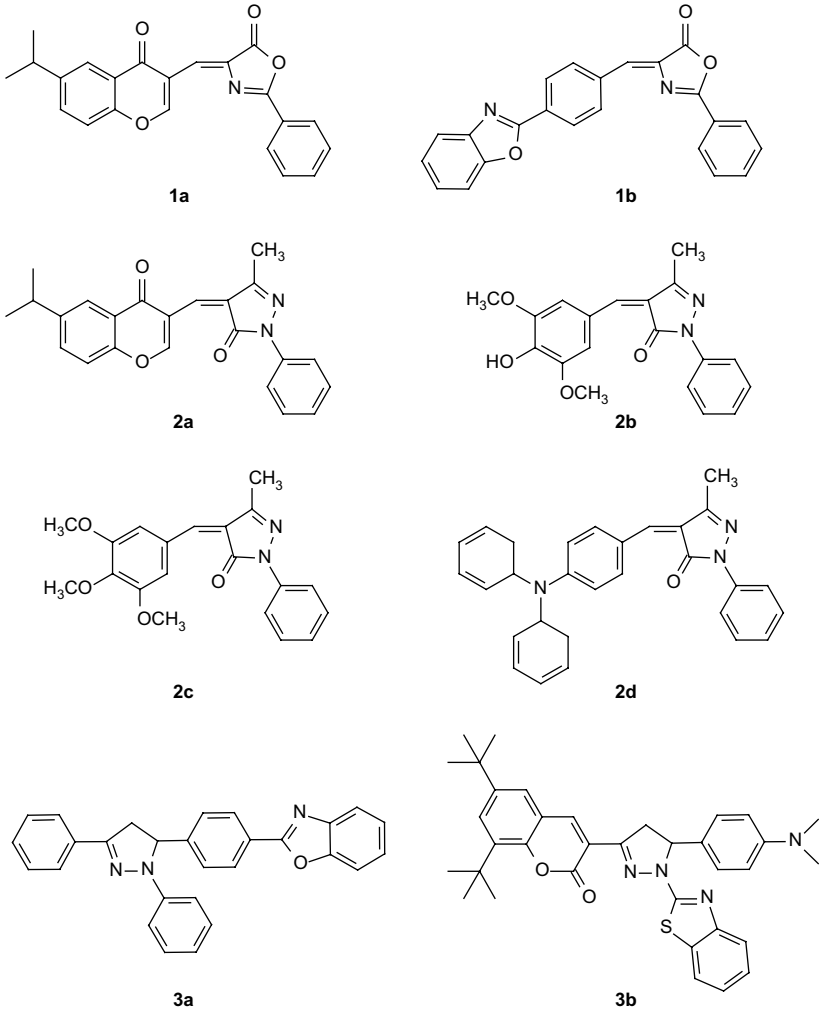

Fig. 3. The molecular structures of the heterocycle chromophores.

Table 1
Crystal data and structure refinement for **2b** and **2d**

Empirical formula	$C_{19}H_{18}N_2O_4$	$C_{29}H_{23}N_3O$
Formula weight	338.35	429.50
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	11.047(2)	12.539(3)
b (Å)	7.4630(15)	18.787(4)
c (Å)	20.377(4)	9.7080(19)
α (°)	90.00	90.00
β (°)	97.35(3)	93.03(3)
γ (°)	90.00	90.00
Volume (Å^3), Z	1666.2(6), 4	2283.7(8), 4
D_{calc} (Mg/m^3)	1.349	1.249
Absorption coefficient (mm^{-1})	0.096	0.077
F (0 0 0)	712	904
Crystal size (mm)	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20
θ range for data collection (°)	1.86–25.18	1.63–25.21
Limiting indices	$0 \le h \le 13$ $0 \le k \le 8$ $-24 \le l \le 24$	$-14 \le h \le 14$ $0 \le k \le 22$ $0 \le l \le 11$
Reflections collected/unique	3139/2975 [$R_{int} = 0.0319$]	4367/4109 [$R_{int} = 0.0419$]
Max. and min. transmissions	0.9905 and 0.9718	0.9848 and 0.9699
Data/restraints/parameters	2975/0/227	4109/0/298
Goodness-of-fit on F^2	1.001	1.001
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0540$, $wR_2 = 0.1398$	$R_1 = 0.0672$, $wR_2 = 0.1438$
R indices (all data)	$R_1 = 0.0829$, $wR_2 = 0.1791$	$R_1 = 0.1225$, $wR_2 = 0.1940$
Extinction coefficient	0.016(3)	
Largest diff. peak and hole (eÅ^{-3})	0.222 and −0.216	0.254 and −0.234
CCDC	689218	689217

$J = 8.1$ Hz, 2H), 8.57 (d, $J = 8.9$ Hz, 2H). IR (KBr) ν: 1676, 1619, 1575, 1558, 1542, 1488, 1438, 1317, 1230, 1191, 1127, 996, 831, 759, 696, 666, 514 cm^{-1}. MS m/z: 430.5 (M + 1). Anal. calcd for $C_{29}H_{23}N_3O$: C 81.09, H 5.40, N 9.78; found: C 81.23, H 5.67, N 9.53.

2.2.3. General procedure for the synthesis of pyrazoline derivatives *3a* and *3b*

A mixture of appropriate chalcone (2 mmol), phenylhydrazine (or 2-hydrazino-1,3-benzothiazole) (2.2 mmol) in ethylene glycol (20 mL) was irradiated in a microwave oven for an optimized time according to the above mentioned method. Then the reaction mixture was poured into water. The solid product was filtrated, dried and recrystallized from EtOH–DMF.

*2.2.3.1. 5-(4-(Benzoxazol-2-yl)phenyl)-1,3-diphenyl-2-pyrazoline (**3a**).* Yellow solid, yield 66%; mp 235–237 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ: 3.21 (dd, $J = 7.4$, 17.1 Hz, 1H), 3.93 (dd, $J = 12.4$, 17.1 Hz, 1H), 5.37 (dd, $J = 7.4$, 12.4 Hz, 1H), 6.83 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 7.9$ Hz, 2H), 7.22 (t, $J = 8.0$ Hz, 2H), 7.34–7.45 (m, 5H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.57–7.81 (m, 4H), 8.25 (d, $J = 8.3$ Hz, 2H). IR (KBr) ν: 1618, 1598, 1555, 1499, 1491, 1453, 1390, 1320, 1244, 1114, 1054, 1012, 875, 832, 815, 748, 690 cm^{-1}. MS m/z: 416.5 (M + 1). Anal. calcd for $C_{28}H_{21}N_3O$: C 80.94, H 5.09, N 10.11; found: C 80.72, H 5.17, N 9.87.

*2.2.3.2. 1-(Benzothiazol-2-yl)-3-(6,8-di-*tert*-butyl-2-oxo-2*H*-1-benzopyran-3-yl)-5-(4-*N,N*-dimethylaminophenyl)-2-pyrazoline (**3b**).* Yellow solid, yield 59%; mp 271–273 °C. ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ: 1.39 (s, 9H), 1.53 (s, 9H), 2.94 (s, 6H), 3.61 (dd, $J = 5.1$, 18.7 Hz, 1H), 4.13 (dd, $J = 11.9$, 18.6 Hz, 1H), 5.75 (dd, $J = 5.1$, 12.0 Hz, 1H), 6.67 (d, $J = 8.8$ Hz, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.25–7.30 (m, 3H), 7.47 (s, 1H), 7.57–7.65 (m, 3H), 8.53 (s, 1H). IR (KBr) ν: 1717, 1614, 1599, 1538, 1482, 1443, 1346, 1285, 1223, 1136, 1015, 879, 810, 749, 721, 694 cm^{-1}. MS m/z: 579.8 (M + 1). Anal. calcd for $C_{35}H_{38}N_4O_2S$: C 72.63, H 6.62, N 9.68; found: C 72.49, H 6.75, N 9.51.

2.3. X-ray crystallography

Suitable single crystals of **2b** and **2d** for X-ray structural analysis were obtained by evaporation of ethanol solution. The diffraction data for both structures were collected with an Enraf-Nonius CAD-4 diffractometer using a graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures were solved by direct methods with SHELXS-97 program and refinements on F^2 were performed with SHELXL-97 program by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C–H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The hydroxyl H atom was treated as a riding atom, with O–H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. All other H atoms were placed in geometrically

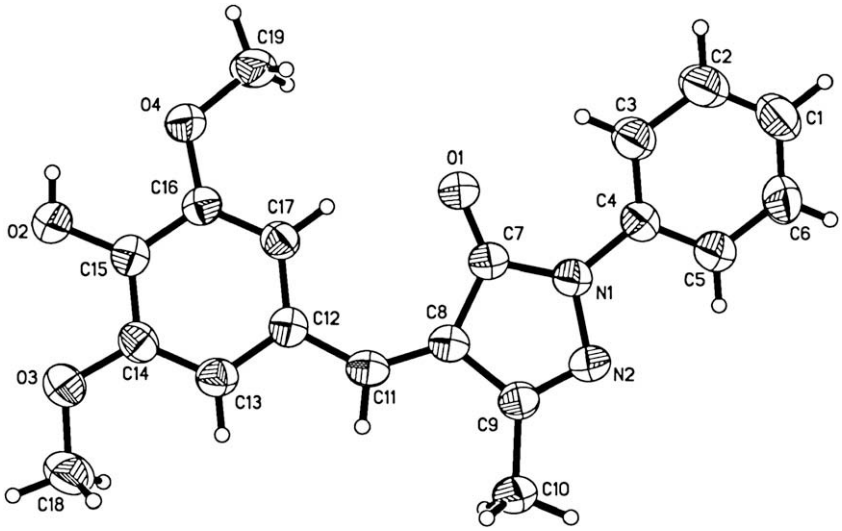

Fig. 4. The molecular structure of **2b**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

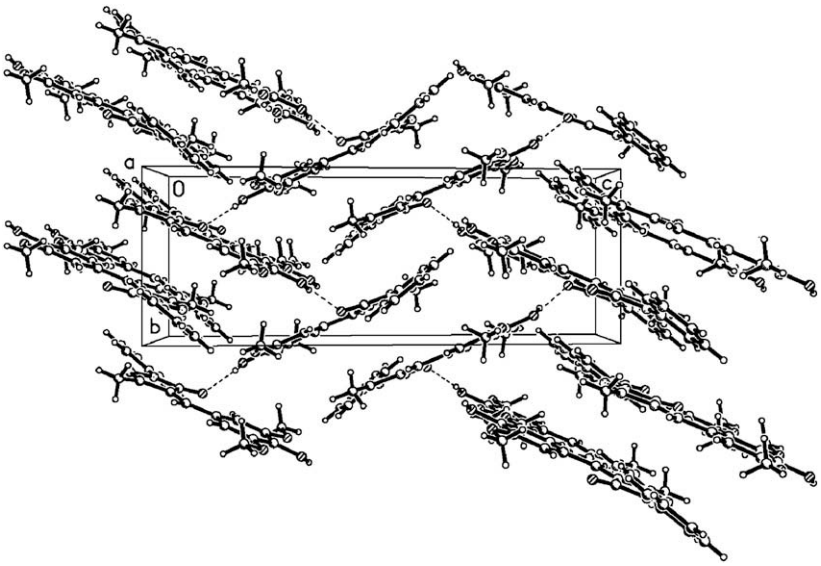

Fig. 5. A packing diagram for **2b**, viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

idealized positions and constrained to ride on their parent atoms, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. A summary of the crystallographic data and structure refinement details is given in Table 1.

3. Results and discussion

3.1. Synthesis

The 6-isopropyl-3-formyl-chromone and chalcone derivatives, which are important starting material in the synthesis of the target heterocycles, were prepared using the literature procedures [20,21]. The oxazolones (**1**) were prepared as depicted in Fig. 1. The properly substituted aryl or heteroaryl aldehydes were reacted with a slight excess of hippuric acid in the presence of acetic anhydride and anhydrous sodium acetate under microwave irradiation, to afford the oxazolones (**1**) in 49–56% yields.

When the properly substituted aryl or heteroaryl aldehydes were treated with 3-methyl-1-phenyl-pyrazol-5-one in ethylene glycol by microwave irradiation, the pyrazolone derivative **2** was obtained in 43–67% yields (Fig. 1).

On the other hand, reaction of 3-(4-(benzoxazol-2-yl)phenyl)-1-phenylprop-2-en-1-one with excess phenylhydrazine was carried out in ethylene glycol under microwave irradiation to give pyrazoline **3a** in 66% yield (Fig. 2). A similar treatment yields pyrazoline **3b** by the condensation of 6,8-di-*tert*-butyl-3-(3-(4-*N*,*N*-dimethylamino phenyl)-prop-2-enoyl)-2*H*-1-benzopyran-2-one and 2-hydrazino-1,3-benzothiazole, in ethylene glycol under microwave irradiation (Fig. 2). This reaction probably takes place through mediation of an appropriate α,β-unsaturated hydrazone, which immediately cyclizes to give a pyrazoline ring under microwave irradiation condition.

It is noteworthy that such a microwave procedure for rapid preparation of various oxazolones, pyrazolones and pyrazolines affords advantages of short reaction time, moderate yields and simple workup.

The assumed structures of compounds **1**–**3** were proved by IR and ^{1}H NMR spectra. The IR spectra of compounds **1** showed two

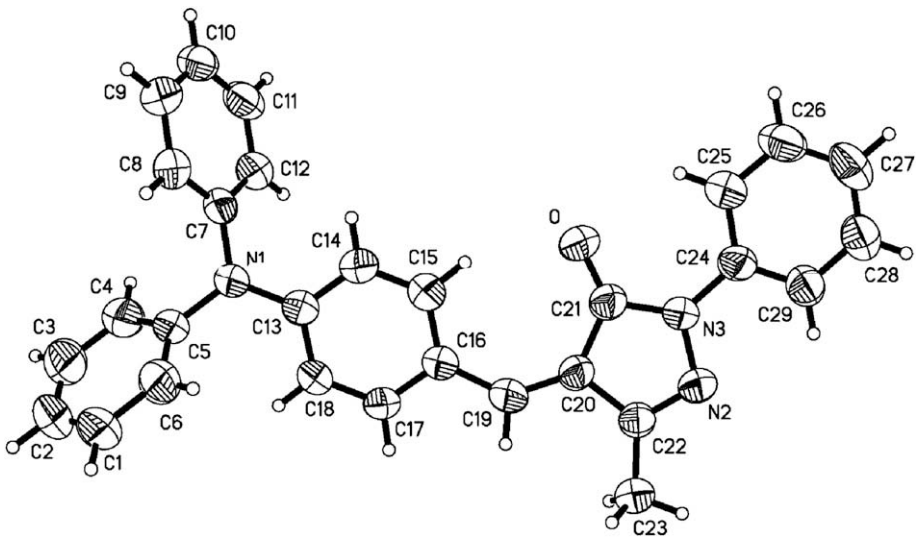

Fig. 6. The molecular structure of **2d** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

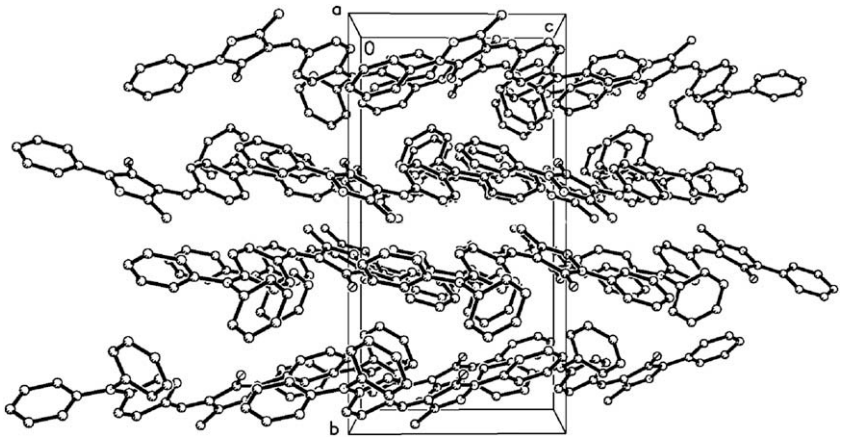

Fig. 7. A packing diagram for **2d**, viewed down the *a* axis. H atoms are omitted for clarity.

strong bands at 1792–1796 and 1649–1652 cm^{-1} due to C═O lactone and C═C double bond, respectively, indicating the formation of oxazolone backbone. The C═O stretching vibrations of the carbonyl groups of **2** exhibited strong absorption bands at 1656–1688 cm^{-1} belonging to the *ν*(C═O) of the pyrazolone ring.

Compared with the IR spectrum of 6,8-di-*tert*-butyl-3-(3-(4-*N*,*N*-dimethylamino phenyl)-prop-2-enoyl)-2*H*-1-benzopyran-2-one (1725 and 1655 cm^{-1}), compound **3b** displayed disappearance of band at around 1655 cm^{-1} due to C═O of chalcone, which clearly confirmed that a cyclocondensation with 2-hydrazino-1,3-benzothiazole had taken place. Strong band at around 1717 cm^{-1} revealed the presence of coumarin nucleus.

The structures of the prepared compounds were also confirmed by ^{1}H NMR spectra. The signals of protons displayed chemical shifts and multiplicities corresponding to their surroundings. The ^{1}H NMR spectra of **1** and **2** display the signals of the olefinic proton in the 7.46–8.06 ppm range. Moreover, the ^{1}H NMR spectra of **1a** and **2a** showed a well distinguishable intensive singlet signal at $\delta = 9.76$–10.83 ppm for proton at C-2 position of the chromone. Such a signal is characteristic for chromone system protons if the chromone ring is substituted by strong electron withdrawing group at 3-position.

In the ^{1}H NMR spectra of compounds **3** signals of the CH_2–CH fragment of the pyrazoline ring were present. These protons appear as three doublets of doublets, respectively, in the $\delta = 3.18$–3.64, 3.89–4.17 and 5.34–5.79 ppm regions, each integrating for one proton. The complete chemical shifts for all compounds are listed in Section 2.

In addition, the formation of the oxazolones is highly selective towards the *Z*-isomer and final crystallization gave pure *Z*-isomers of the oxazolones. For example, syringaldehyde and 3,4,5-trimethoxybenzaldehyde give oxazolones as Z configuration [16,17]. Also, the *Z* configuration of the olefinic bond of compounds **2b** and **2d** was established by X-ray diffraction crystal structure analysis in this work. Therefore, based on these observations, it could be expected that compounds **1a**, **1b**, **2a** and **2c** might also adopt a Z configuration about the central olefinic bond in the solid state. However, it should be pointed out that more experiments must be carried out to estimate such hypothesis.

3.2. Crystal structure

As can be seen from Fig. 4, the molecule of compound **2b** adopts a *Z* configuration about the central olefinic bond. The central pyrazole ring (N1/N2/C7–C9) is essentially planar, with an r.m.s deviation of 0.0090 Å for the fitted atoms. The pyrazole ring, the olefinic bond and the substituted phenyl ring (C12–C17) are almost coplanar [r.m.s. deviation = 0.0175 Å, maximum deviation = −0.0425(4) Å for atom C7], which allows conjugation. However, a dihedral angle of 21.4(2)° is found between the mean planes of the pyrazole ring and the C1–C6 phenyl ring. Also, O2–O4, C18 and

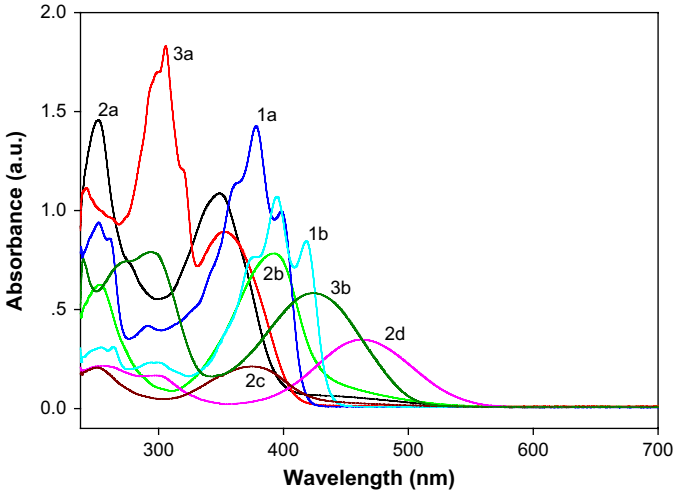

Fig. 8. Absorption spectra of the heterocycle chromophores in chloroform solution.

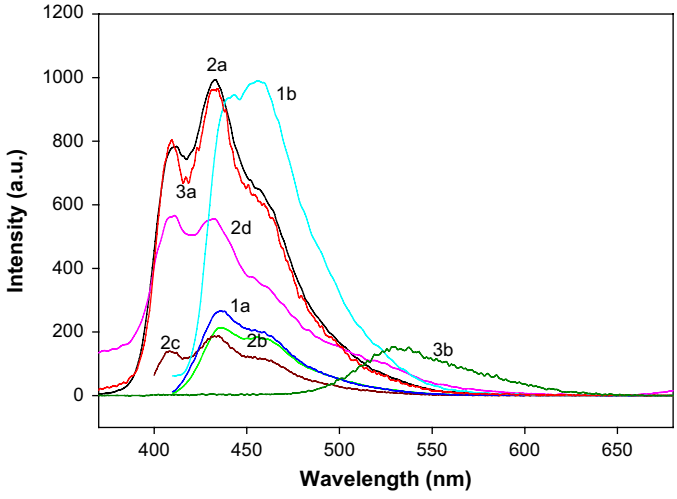

Fig. 9. Fluorescence spectra of the heterocycle chromophores in chloroform solution.

C19 are approximately coplanar with their attached benzene ring. This is in marked contrast to the orientations in other pyrazole derivatives [18,19], in which the planes of the three phenyl rings all twist out of the pyrazole plane.

Obviously, the bond length of C8–C11 (1.368(4) Å) is in good agreement with a carbon–carbon double bond. Moreover, the bond lengths of C7–C8 (1.481(4) Å), C8–C9 (1.443(4) Å) and C11–C12 (1.441(4) Å) are, as expected, shorter than a normal carbon–carbon single bond due to a conjugation effect. Therefore, it could be suggested that the C12–C17 phenyl ring is highly conjugated with the pyrazole ring.

The molecules are linked together by intermolecular O–H···O (O2–H2B···O1^{i}: O–H = 0.82 Å, H2B···O1 = 2.08 Å, O2···O1 = 2.853(3) Å, O2–H2B···O1 = 156.4°; symmetry code: (i) $-x+1$, $y+1/2$, $-z+1/2$) hydrogen bonds into a *zigzag* one-dimensional chain along the *b*-axis (Fig. 5).

The molecule structure of **2d** is shown in Fig. 6. Like molecule **2b**, in **2d** also, the molecule adopts a *Z* configuration about the central olefinic bond and the pyrazole ring is planar. The dihedral angles between the pyrazole ring plane and the C13–C18 and C24–C29 phenyl ring planes are 9.2(3) and 6.0(3)°, respectively. Therefore, apart from the two phenyl rings (C5 and C7), the rest of the molecule is nearly coplanar.

On the other hand, the three aryl rings of the triphenylamine moiety show no coplanar structure. At the diphenylamino donor end, the central nitrogen (N1) and its three bended carbon (C5, C7 and C13) atoms are basically coplanar, forming a quasi-equilateral trigonal NC3 plane, with the sum of the three C–N–C angles (359.9°) being very close to 360°. Moreover, around the central nitrogen, three phenyl ring planes are arranged in a propeller-like fashion. Similar geometry has been observed in related triarylamine analogues [21].

The linkage between pyrazolone system and phenyl ring (C16) is quite conjugated with bond lengths of C16–C19: 1.432(5) Å and C19–C20: 1.352(5) Å, suggesting that all non-hydrogen atoms between donor and acceptor are highly conjugated, leading to a π-bridge for the charge transfer from amino to pyrazolone system. The molecules are assembled to form a layer structure (Fig. 7).

3.3. Absorption and fluorescence spectra

The structures of the target molecules are shown in Fig. 3. Molecules **1a**, **1b** and **2a** consist of a typical A-π-A structure, while **2b**–**2d** consist of a typical D-π-A structure. UV–vis absorption spectra of these molecules in diluted chloroform solutions are given in Fig. 8. Several absorption peaks could be observed in the linear absorption spectra of all molecules in the wavelength range from 237 to 600 nm, while almost no linear absorption was observed beyond 600 nm. It can be seen from Fig. 8 that, the spectral shape of **1a** is very similar to that of **1b**. The maximum absorption peaks are red-shifted from **1a** (378 nm) to **1b** (395 nm). The 4-(benzoxazol-yl)phenyl system caused a bathochromic effect of approximately 17 nm relative to the chromone system, suggesting that the conjugation of 4-(benzoxazol-yl) phenyl system is larger than that of chromone skeleton. As a result, the red shift of absorption can possibly occur. At the same time, the multi-peak profiles in the linear absorption spectra of **1** indicate that molecules in the excited state suffer structure distortions in the π-conjugated frameworks [21].

In the case of **2**, the similar spectral shape was also observed, because these compounds possess a similar structure. For the maximum absorption peaks of the first absorption band of **2**, there is a consequence: **2d** > **2b** > **2c** > **2a** (Fig. 8). It could be found that λ_{max} of **2b** is larger than that of **2c**, although **2c** is very similar to **2b** in the structure. Moreover, the maximum absorption peaks of the first absorption band of **2** are red-shifted from **2a** (349 nm) to **2c** (375 nm), to **2b** (393 nm), and to **2d** (463 nm). When replacing chromon-3-yl acceptor with a 3,4,5-trisubstitutedphenyl donor in one terminal moiety of the pyrazolone molecules, a bathochromic effect of approximately 26–44 nm is observed. Furthermore, replacement of chromon-3-yl acceptor with a triphenylamine group resulted in a strong bathochromic shift (114 nm). The results above imply that more π-electrons and longer π-conjugated structure may be involved in **2d** than those in others.

Additionally, it could be recognized that the first absorption band (λ_{max} = 353 nm) of pyrazoline **3a** (Fig. 8) exhibited a blue-shift of 70 nm compared to that of **3b** (423 nm). It is well known that pyrazoline compounds are typical intra-molecular charge transfer compounds. Thus, this difference might be attributed to the different conjugation degree in these two compounds. Molecule **3b** is of a larger conjugated system than **3a**, because there is a coumarin moiety in 3-position of pyrazoline **3b**, which is involved in the large conjugation (N1 → N2 → C3, 2,3-position of pyrazoline → 3-coumarinyl), and there is a phenyl group in 3-position of pyrazoline **3a** (N1 → N2 → C3, 2,3-position of pyrazoline → 3-phenyl).

Fig. 9 shows the fluorescence spectra for these molecules in diluted chloroform solutions. It can be observed that all heterocycle chromophores are fluorescent in solution. Pyrazoline **3b** presents a green emission of fluorescence, but the other seven compounds have their emission peaks located at ~410–460 nm, indicating that they can emit blue lights. As shown in Fig. 9, the fluorescence spectrum of **1a** has two emission peaks at about 436 and 454.5 nm. As for **1b**, its emission peaks are at 443.5 and 455.5 nm, respectively. The emission peaks of **1b** slightly shift to longer wavelength with respect to that of **1a**.

Moreover, compounds **2a**, **2c**, **2d** and **3a** have similar fluorescence spectra. Especially, the similar shape and position, and two strong emission peaks near 410 and 433 nm, with the shoulder peak at around 456 nm, were observed for these molecules, although they possess different scales or sizes in conjugated system. However, the structural modification obviously causes difference in fluorescence peak intensity.

In the case of **2b**, the fluorescence spectrum is very similar to that of **1a**, but obviously different from those of its analogues (**2a**, **2c** and **2d**) due to the absence of emission peak at 410 nm. Moreover, the maximum emission peak of **2b** was red-shifted to 436.5 nm, when compared to **2a**, **2c**, and **2d**, but blue-shifted by about 7 nm with respect to that of **1a**.

In contrast, only an emission peak, at around 529 nm, could be observed in the fluorescence spectrum of molecule **3b**, which indicates that the emission occurs from the lowest excited state with the largest oscillator strength [22]. Significant red-shift can be noticed by changing from molecules **3a** to **3b**, which is similar to that in the linear absorption and can be attributed to the larger conjugated structure of **3b**. Also, it should be noted that compounds **3a** and **3b** both have a non-conjugated substituted phenyl group at the 5-position of pyrazoline. It is impossible to have a coplanar structure with the pyrazoline moiety and this makes these molecules difficult to crystallize. This is an important property for the film materials used in any device, because the crystallization of glassy state is the main cause for the degradation of device [23].

4. Conclusions

The new oxazolones **1a** and **1b**, pyrazolones **2a**–**2d** and pyrazolines **3a** and **3b** heterocyclic chromophores have been synthesized and characterized. The crystal structures of **2b** and **2d** were investigated by single crystal X-ray crystallography. The absorption and emission spectra of these molecules were measured in chloroform solution. It was found that new heterocyclic chromophores

are fluorescent in solution. Compounds **1**, **2** and **3a** emitted blue light (410–460 nm), while **3b** emitted green light (529 nm).

These heterocyclic chromophores could be potential optical materials for some fields, such as OLED materials, two-photon absorption materials, as well as biosensors or fluorescent probes in biological applications. Further research is presently under study in our laboratory.

5. Supplementary material

The crystallographic data (excluding structure factors) of **2b** and **2d** have been deposited with the Cambridge Crystallographic Center as supplementary publication no. CCDC 689217 and 689218. Copy of this information may be obtained free of charge via www: http://www.ccdc.cam.ac.uk or from The Director, CCDC, 12 Union Road, Cambridge CB221EZ, UK (fax: +44 1223 336033; email: deposite@ccdc.cam.ac.uk). Structural factors are available on request from the authors.

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