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The synthesis, X-ray crystal structure and optical properties of novel 1,3,5-triaryl pyrazoline derivatives

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ABSTRACT

A series of novel 1,3,5-triaryl pyrazoline derivatives has been synthesized by the reaction of chalcone and 3-chloro-6-hydrazinylpyridazine in 47–82% yields. The structures of compounds obtained were determined by IR, ^{1}H NMR and HRMS spectra. Representatively, the spatial structure of compound **3d** was determined by using X-ray diffraction analysis. Absorption and fluorescence spectral characteristics of the compounds were investigated in $CHCl_3$ by UV–vis absorption and emission spectra. The results showed that the absorption maxima of the compounds vary from 332 to 342 nm depending on the group bonded to benzene rings. The maximum emission spectra of compounds in $CHCl_3$ are dependent on groups in benzene ring in which a strong electron-donating group in benzene ring such as methoxyl group on C3 position of pyrazoline made the emission wavelength of **3e**, **3f** and **3g** red shifted than that of compounds **3b**, **3c** and **3d** with chlorine group. The intensity of absorption and fluorescence was also correlated with substituent on two aryl rings. In addition, the absorption spectra of these compounds change very little with increasing solvent polarity.

1. Introduction

Pyrazoline derivatives are attracting increasing interest of many researchers, not only in medicinal chemistry because of their bioactivity such as antimicrobial [1,2], antiamoebic [3,4], antinociceptive [5], anticancer [6], antidepressant [7] and anti-inflammatory [8–12], but also in conjugated fluorescent dyes emitting blue fluorescence with high fluorescence quantum yield [13,14] and electroluminescence fields [15–17]. Attempts have been made to synthesize and elucidate the effects of substituent on the absorption and fluorescence properties of this class of compounds [18–23].

The design and synthesis of fluorescent small molecules with desirable properties are of considerable current interest in biology research. The advent of sensitive fluorescence detectors has enabled advances in biological imaging and the emergence of the field of single molecule spectroscopy [24,25]. To date there have been relatively few studies of the cellular localization of agents in which small molecule is linked to a fluorophore, such as coumarin [26,27]. Thus, in continuation of our efforts in synthesizing various bioactive molecules [28–33], we would like to synthesize novel small molecules with both potential bioactivity and fluorescent property.

2. Materials and methods

2.1. General

Thin-layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA). ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on an XD-4 digital micro melting point apparatus. IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were recorded on a Q-TOF6510 spectrograph (Agilent). UV–vis spectra were recorded on a U-4100 (Hitachi). Fluorescent measurements were recorded on a Perkin-Elmer LS-55 luminescence spectrophotometer.

2.2. General procedure for the synthesis of compound **3**

To a stirred solution of substituted chalcone (**1**) (1.0 mmol) in ethanol (15 mL) was added 3-chloro-6-hydrazinylpyridazine (**2**) (1.2 mmol) and NaOH (2.0 mmol) and the reaction mixture was refluxed for 3–6 h as shown in Scheme 1. The progress of the reaction was monitored by TLC. After completion, the reac-

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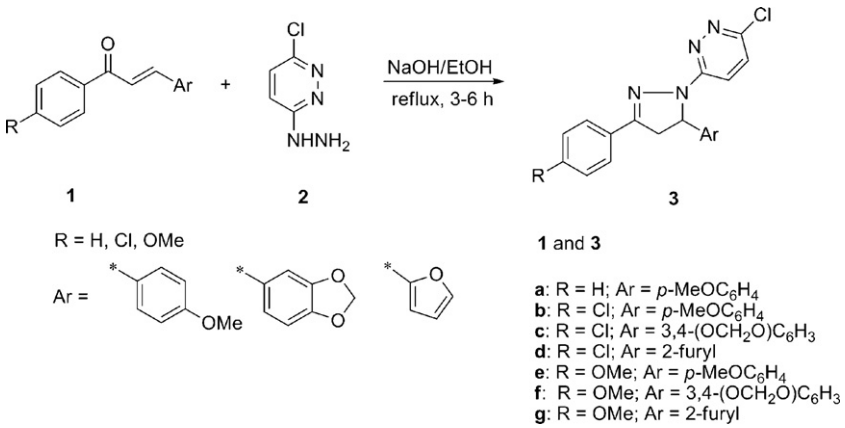


Scheme 1. Synthesis of 1,3,5-triaryl pyrazoline derivatives.

tion mixture was cooled to room temperature and the precipitate was filtered, washed with ethanol and water, and dried to give pure **3**.

2.3. The spectroscopic data of compound *3*

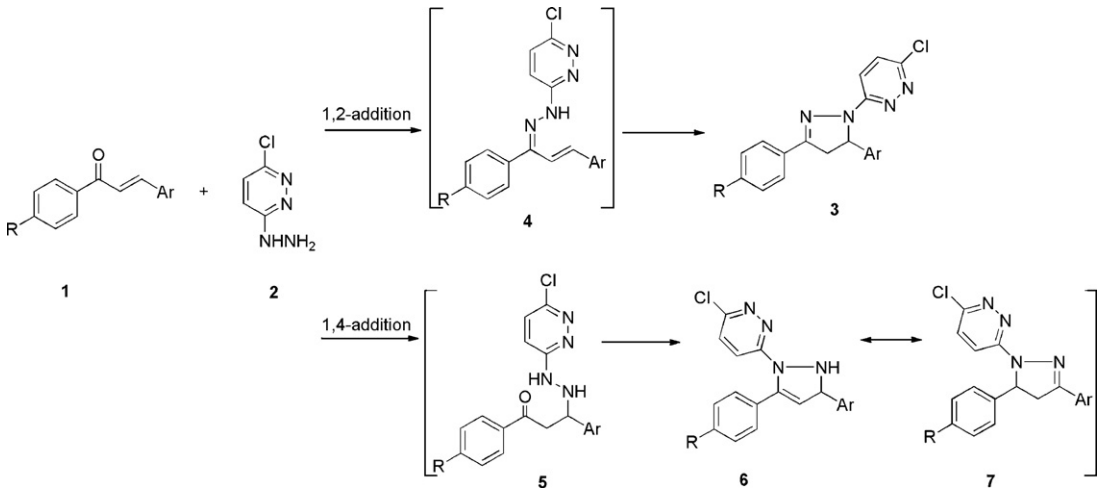
3-Chloro-6-(5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl) pyridazine (**3a**). Pale yellow solid, yield 64%; mp 186–187 °C; IR (KBr, cm^{-1}) 1580.6 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.31 (dd, 1H, J = 5.3, 17.6 Hz, $4H_{trans}$), 3.75 (s, 3H, OCH_3), 3.87 (dd, 1H, J = 12.1, 17.6 Hz, $4H_{cis}$), 5.82 (dd, 1H, J = 5.3, 12.1 Hz, 5H of pyrazoline), 6.80 (d, 2H, J = 8.6 Hz, Ar-H), 7.23 (d, 1H, J = 9.4 Hz, pyridazine-H), 7.24 (d, 2H, J = 8.3 Hz, Ar-H), 7.39–7.46 (m, 3H, Ar-H), 7.70 (d, 1H, J = 9.4 Hz, pyridazine-H), 7.76 (d, 2H, J = 8.6 Hz, Ar-H); HRMS: calcd. for $[M+H]^+$ $C_{20}H_{18}ClN_4O$: 365.1169; found: 365.1169.

3-Chloro-6-(3-(4-chlorophenyl)-5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl) pyridazine (**3b**). Pale yellow solid, yield 70%; mp 180–181 °C; IR (KBr, cm^{-1}) 1578.5 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.27 (dd, 1H, J = 5.4, 17.6 Hz, $4H_{trans}$), 3.75 (s, 3H, OCH_3), 3.84 (dd, 1H, J = 12.2, 17.6 Hz, $4H_{cis}$), 5.83 (dd, 1H, J = 5.4, 12.2 Hz, 5H of pyrazoline), 6.8 (d, 2H, J = 8.6 Hz, Ar-H), 7.23 (d, 1H, J = 8.6 Hz, pyridazine-H), 7.24 (d, 2H, J = 8.5 Hz, Ar-H), 7.40 (d, 2H, J = 8.4 Hz, Ar-H), 7.68 (d, 3H, J = 8.6 Hz, pyridazine-H and Ar-H); HRMS: calcd. for $[M+H]^+$ $C_{20}H_{17}Cl_2N_4O$: 399.0779; found: 399.0781.

3-(5-(Benzo[d][1,3]dioxol-5-yl)-3-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-1-yl)-6-chloropyridazine (**3c**). Pale yellow solid, yield 68%; mp 183–184 °C; IR (KBr, cm^{-1}) 1579.2 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.24 (dd, 1H, J = 5.1, 17.5 Hz, $4H_{trans}$), 3.83 (dd, 1H, J = 12.1, 17.5 Hz, $4H_{cis}$), 5.79 (dd, 1H, J = 5.1, 12.1 Hz, 5H of pyrazoline), 5.89 (s, 2H, OCH_2O), 6.71 (d, 2H, J = 7.9 Hz, Ar-H), 6.81 (d, 1H, J = 7.9 Hz, Ar-H), 7.26 (d, 1H, J = 9.3 Hz, pyridazine-H), 7.39 (d, 2H, J = 8.5 Hz, Ar-H), 7.67 (d, 2H, J = 8.7 Hz, Ar-H), 7.69 (d, 1H, J = 9.3 Hz, pyridazine-H); HRMS: calcd. for $[M+H]^+$ $C_{20}H_{15}Cl_2N_4O_2$: 413.0572; found: 413.0569.

3-Chloro-6-(3-(4-chlorophenyl)-5-(furan-2-yl)-4,5-dihydro-1H-pyrazol-1-yl) Pyridazine (**3d**). Pale yellow solid, yield 82%; mp 243–244 °C; IR (KBr, cm^{-1}) 1582.2 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.56 (dd, 1H, J = 5.4, 17.3 Hz, $4H_{trans}$), 3.69 (dd, 1H, J = 11.9, 17.3 Hz, $4H_{cis}$), 6.00 (dd, 1H, J = 5.4, 11.9 Hz, 5H of pyrazoline), 6.28 (dd, 1H, J = 1.7, 3.2 Hz, furan-H), 6.43 (d, 1H, J = 3.2 Hz, furan-H), 7.27 (d, 1H, J = 1.7 Hz, furan-H), 7.27 (d, 1H, J = 9.3 Hz, pyridazine-H), 7.40 (d, 2H, J = 8.6 Hz, Ar-H), 7.66 (d, 1H, J = 9.3 Hz, pyridazine-H), 7.70 (d, 2H, J = 8.6 Hz, Ar-H); HRMS: calcd. for $[M+H]^+$ $C_{17}H_{13}Cl_2N_4O$: 359.0466; found: 359.0467.

3-(3,5-Bis(4-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)-6-chloropyridazine (**3e**). Pale yellow solid, yield 47%; mp 121–123 °C; IR (KBr, cm^{-1}) 1582.6 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.29 (dd, 1H, J = 5.0, 17.5 Hz, $4H_{trans}$), 3.75 (s, 3H, OCH_3 of 5-benzene), 3.81 (dd, 1H, J = 12.0, 17.5 Hz, $4H_{cis}$), 3.86 (s, 3H, OCH_3 of 3-benzene), 5.79 (dd, 1H, J = 5.0, 12.0 Hz, 5H of pyrazoline), 6.80 (d, 2H, J = 8.5 Hz, Ar-H), 6.94 (d, 2H, J = 8.6 Hz, Ar-H), 7.22 (d, 1H, J = 9.0 Hz, pyridazine-H), 7.24 (d, 2H, J = 8.6 Hz, Ar-H), 7.67 (d, 1H, J = 9.0 Hz, pyridazine-H), 7.69 (d, 2H, J = 8.5 Hz, Ar-H); HRMS: calcd. for $[M+H]^+$ $C_{21}H_{20}ClN_4O_2$: 395.1275; found: 395.1287.



Scheme 2. A proposed mechanism for the reaction of chalcone and 3-chloro-6-hydrazinylpyridazine.

3-(5-(Benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)-6-chloropyridazine (**3f**). Pale yellow solid, yield 73%; mp 150–151 °C; IR (KBr, cm^{-1}) 1572.9 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.24 (dd, 1H, J = 5.3, 17.5 Hz, $4H_{trans}$), 3.83 (dd, 1H, J = 12.0, 17.5 Hz, $4H_{cis}$), 3.86 (s, 3H, OCH_3), 5.75 (dd, 1H, J = 5.3, 12.0 Hz, 5H of pyrazoline), 5.89 (s, 2H, OCH_2O), 6.71 (d, 1H, J = 8.0 Hz, Ar-H), 6.74 (d, 1H, J = 1.3 Hz, Ar-H), 6.82 (dd, 1H, J = 1.3, 8.0 Hz, Ar-H), 6.94 (d, 2H, J = 8.8 Hz, Ar-H), 7.23 (d, 1H, J = 9.4 Hz, pyridazine-H), 7.68 (d, 1H, J = 9.6 Hz, pyridazine-H), 7.69 (d, 2H, J = 9.0 Hz, Ar-H); HRMS: calcd. for $[M+H]^+$ $C_{21}H_{18}ClN_4O_3$: 409.1067; found: 409.1067.

3-Chloro-6-(5-(furan-2-yl)-3-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl) Pyridazine (**3g**). Yellow solid, yield 78%; mp 193–195 °C; IR (KBr, cm^{-1}) 1580.8 (C=N); ^1H NMR (400 MHz, $CDCl_3$): δ 3.56 (dd, 1H, J = 5.6, 17.2 Hz, $4H_{trans}$), 3.69 (dd, 1H, J = 11.8, 17.2 Hz, $4H_{cis}$), 3.86 (s, 3H, OCH_3), 5.96 (dd, 1H, J = 5.6, 11.8 Hz, 5H of pyrazoline), 6.27 (dd, 1H, J = 1.8, 3.2 Hz, furan-H), 6.41 (d, 1H, J = 3.2 Hz, furan-H), 6.95 (d, 2H, J = 8.8 Hz, Ar-H), 7.24 (d, 1H, J = 9.4 Hz, pyridazine-H), 7.26 (d, 1H, J = 1.8 Hz, furan-H), 7.65 (d, 1H, J = 9.4 Hz, pyridazine-H), 7.71 (d, 2H, J = 8.8 Hz, Ar-H); HRMS: calcd. for $[M+H]^+$ $C_{18}H_{16}ClN_4O_2$: 355.0962; found: 355.0962.

2.4. X-ray crystallography

Suitable single crystals of **3d** for X-ray structural analysis were obtained by slow evaporation of a solution of the solid in dichloromethane at room temperature for 7 days. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 298(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 Uiso(H) = 1.5 Ueq(C). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.93 Å and Uiso(H) = 1.2 Ueq(C).

3. Results and discussion

3.1. Synthesis of compound 3

The synthetic routes of the proposed compound **3** are outlined in Scheme 1. Starting chalcone **1** can be easily prepared by Claisen–Schmidt condensation between acetophenone and aromatic aldehydes in the presence of ethanolic solution of sodium hydroxide according to the literatures [4]. The 3,5-diaryl pyrazoline derivatives **3a–g** were obtained by the reaction of chalcone **1** with 3-chloro-6-hydrazinylpyridazine **2** at reflux condition in 47–82% yields. It is noticed that the regioselectivity of the reaction of chalcone **1** with 3-chloro-6-hydrazinylpyridazine **2** was satisfied in which we obtained the purpose products rather than isomers. It can be explained by a proposed mechanism of the reaction as shown in Scheme 2. Nitrogen in 3-chloro-6-hydrazinylpyridazine attacked firstly carbonyl carbon with more positive charge and then dehydration took place to form an intermediate **4** that proceeds to afford product **3** (1,2-addition route). In the present condition other isomers **6** or **7** that should be formed by 1,4-addition route are not found. The influences of the substituent in phenyl moiety of chalcone **1** on the yield are consistent with the mechanism. Comparing the yield of **3a**, **3b** and **3e** (64%, 70% and 47%, respectively), we found that the reaction of **2** and **1b** with chloro group had higher yield than that of **1a** or **1e** with hydrogen or methoxyl group, respectively, by reason of difference in electron withdrawing. In addition, it is interesting how to distinguish the isomers. Generally, it is difficult to determine the exact structures of isomers only by spectroscopic date. Fortunately, in present study, the spatial structure of compound **3d** was determined by using X-ray diffraction analysis. Thus, the structures of the products **3** were assigned by the analyses of their spectral data including ^1H NMR, IR and HRMS comparing with X-ray diffraction analysis.

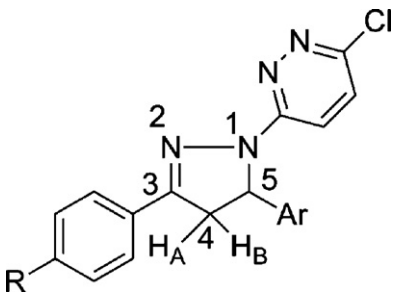


Fig. 1. Structure of compound **3**.

3.2. Structure characterization

The IR spectra of all the compounds showed ν(C=N) stretch at 1573–1582 cm^{-1} consisting with pyrazoline and pyridazine moiety. In the ^1H NMR spectra of pyrazoline that is shown in Fig. 1, protons H_A and H_B that are geminal protons at C4 carbon, appears in the region 3.24–3.56 and 3.69–3.87 ppm as doublet of doublets in all compounds. The CH proton at C5 also appeared as doublet of doublets in the region of 5.75–6.00 ppm due to vicinal coupling with two non-equivalent geminal protons of C4 carbon. Two *ortho*-aromatic protons signals in chloropyridazine moiety appeared at the range of δ = 7.23–7.27 and 7.65–7.70 ppm as doublet peaks (J = 8.7–9.4 Hz), respectively. HRMS showed that found [M+H]-ion peak accorded with calculated value. Moreover, typically, the structure of compound **3d** was confirmed by X-ray diffraction analysis.

3.3. X-ray crystallography

The molecular view of **3d** is shown in Fig. 2. A summary of crystallographic data collection parameters and refinement parameters for **3d** are compiled in Table 1.

The structure of compound **3d** is crystallized in monoclinic space group $P2_1/n$. One benzene moiety, one furan ring and a pyridazine moiety are bonded to the pyrazoline ring at the atoms of C7, C9 and N2, respectively. Consistent with a pronounced electronic interaction, the bond lengths of C4–C7, N2–C14 are significantly

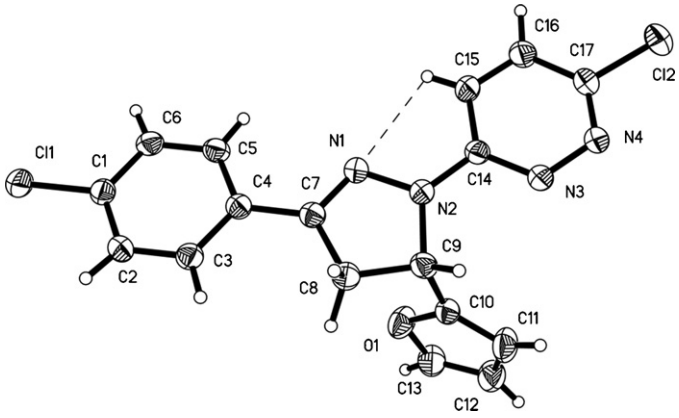


Fig. 2. The molecular structure of compound **3d**, with displacement ellipsoids drawn at the 30% probability level.

Table 1
Summary of crystallographic data and structure refinement details for **3d**.

	3d
Empirical formula	$C_{17}H_{12}C_{12}N_4O_1$
Formula weight	359.21
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.1600(9)$ Å, $\alpha = 90^\circ$ $b = 11.2296(12)$ Å, $\beta = 101.499(2)^\circ$ $c = 17.7512(18)$ Å, $\gamma = 90^\circ$
Volume	1594.0(3) Å^3
Z	4
Calculated density	1.497 Mg/m^3
Absorption coefficient	0.419 mm^{-1}
$F(000)$	736
Crystal size	0.10 mm × 0.10 mm × 0.10 mm
θ range for data collection	2.16–27.54°
Limiting indices	$-10 \le h \le 8$, $-14 \le k \le 14$, $-23 \le l \le 21$
Reflections collected/unique	9225/3608 [R(int) = 0.0300]
Completeness to $\theta = 25.05^\circ$	98.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9593 and 0.9593
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3608/0/265
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0428$, $wR_2 = 0.1173$
R indices (all data)	$R_1 = 0.0673$, $wR_2 = 0.1334$
Largest diff. peak and hole	0.295 and −0.233 e Å^{-3}

shorter as would be expected for a single bond. Moreover, the bond lengths of N1–N2, N1–C7, C7–C8 agree well with the equivalent ones in similar structures [34]. In the crystal of **3d**, torsion angle C14–N2–C9–C10 of −68.83° shows C10 in the pyridazine moiety adopts an *antiperiplanar* conformation with respect to the C14 atom of the benzene ring. In the asymmetry unit, the pyrazoline ring, benzene ring and pyridazine are almost coplanar. And the pyrazoline ring makes dihedral angles with benzene and pyridazine ring of 4.9(1)° and 4.3(1)°, respectively, while the dihedral angle between pyrazoline and furan moiety is 82.6(1)°.

Regarding the crystal structure of **3d**, there is one intramolecular C15–H15···N1 hydrogen bond forming a pseudo five-membered ring. The molecules are connected by weak π···π interactions and further assigned into layers via intramolecular hydrogen bond of C16–H16···Cl1, H16···Cl1 2.73(3) Å, C16···Cl1 3.659(2) Å, C16–H16···Cl1 157(2)° with the symmetry code of $1/2 + x$, $3/2 - y$, $-1/2 + z$, along the *b*-axis (Fig. 3). Besides the aforementioned hydrogen bonds, there is also a weak C–H···π interaction, which is, however, important for the packing modes. Cl1···Cg3 3.6126(12) Å C1···Cg3 4.042(3) Å C1–Cl1···Cg3 91.16(8)°.

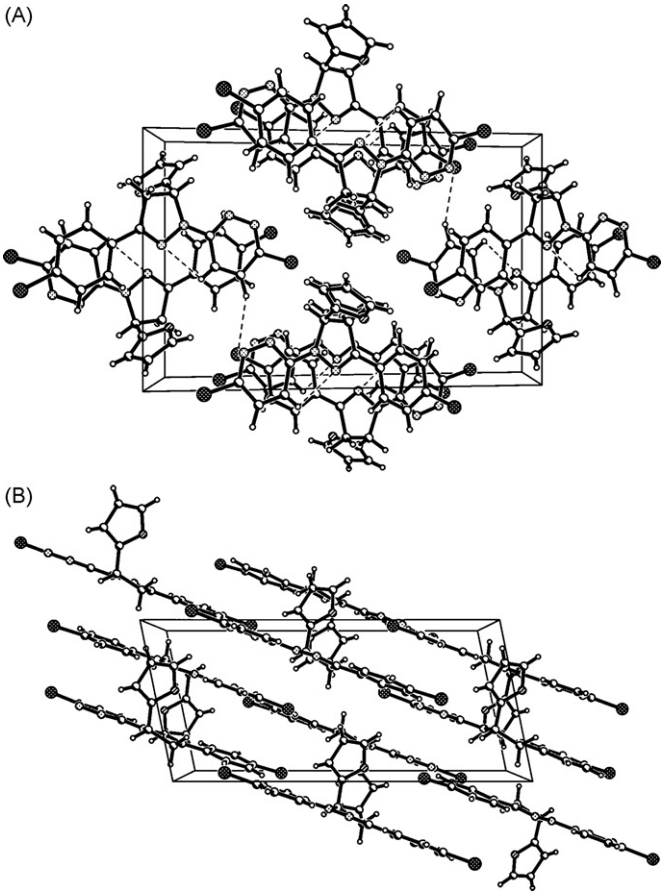


Fig. 3. Crystal packing diagram of **3d** along the *c*-axis (A) and *b*-axis (B). Dashed lines show arrays of hydrogen bonds.

3.4. Absorption spectra

The absorption spectra of compounds **3a**–**g** shown in Fig. 4 and Table 2 have been recorded in chloroform solution with the concentration of 5×10^{-5} M. A small but definite substituent effect was observed such that electron-withdrawing groups (Cl) result in a red shift with respect to an electron-donating group (MeO). The data indicated that, when a chlorine group is located on the phenyl ring at position 3, the absorption peaks of **3b**, **3c** and **3d** are at longer wavelengths than those of **3e**, **3f** and **3g** in which the methoxyl group is bonded. The actual chromophoric π-system is composed of the two aryl substituents in the 1- and 3-position and three out of the five pyrazoline ring atoms (N1–N2–C3). The remaining two carbon atoms (C4 and C5) of the ring are sp^3 hybridized and are not part of the conjugated π-system. The attached aromatic (Ar) in C5 cannot extend to the pi-conjugation system because they are almost perpendicular to π-system, although they are strong electron donor. Thus the λ_{max} depends mainly on the substituent in phenyl.

Furthermore, the absorption intensity was correlated with substituent on two aryl rings. The absorption spectra of representative compounds **3a**, **3b**, **3e** and **3d** in different solvents with the concentration of 5×10^{-5} M are presented in Fig. 5. It was observed that the absorption spectra of these compounds change very little with increasing solvent polarity although there is a tendency of a

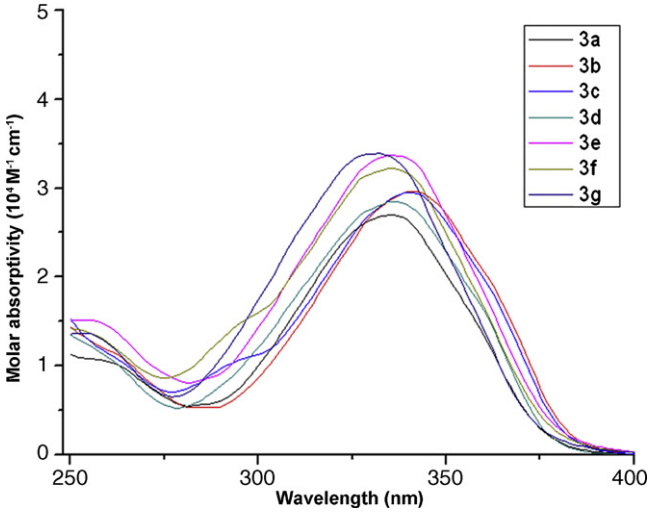


Fig. 4. The UV–vis spectra of pyrazoline derivatives **3a**–**g** in chloroform solution with the concentration of 5×10^{-5} M.

Table 2
Maximum absorption wavelength (λ_{max}) and molar absorptivity (ε_{max}) of pyrazoline derivatives **3a–g** in chloroform.

	Compounds						
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
λ_{max} (nm)	336	342	341	336	336	337	332
ε_{max} ($\times 10^4$ M^{-1} cm^{-1})	2.69	2.95	2.94	2.84	3.36	3.22	3.38

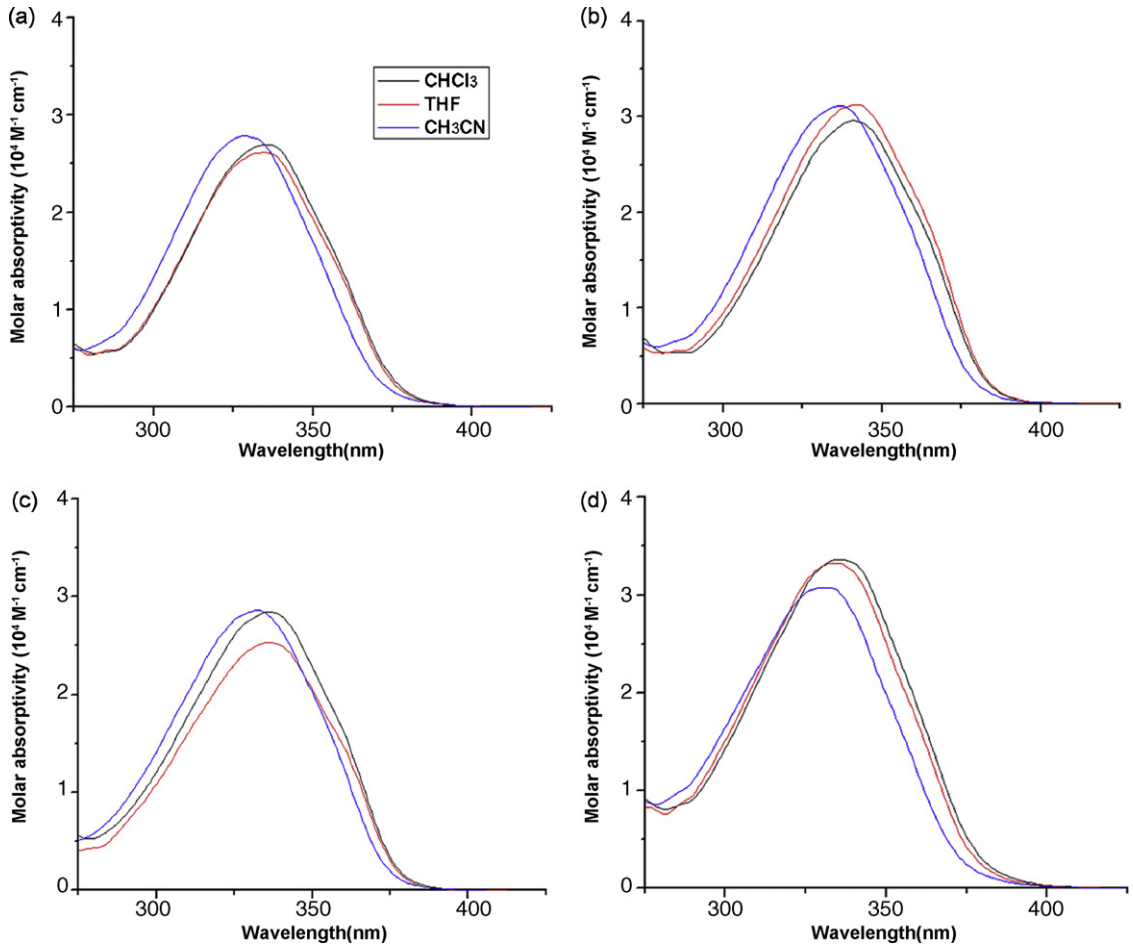


Fig. 5. The UV–vis spectra of **3a**, **3b**, **3e** and **3d** in different solvents with the concentration of 5×10^{-5} M.

shorter λ_{max} in CH_3CN, indicating that there is no charge transfer in the ground state [20] (Table 3).

3.5. Fluorescence

The maximum emission spectra of compounds **3a–g** in $CHCl_3$ are shown in Fig. 6 and Table 4. Their excitation wavelengths were fixed at 329, 339, 332, 327, 335, 335 and 332 nm, respectively. It can be found that their intensity of fluorescence differed from each other. Similar to the absorption spectrum, the group at position 3

Table 3
Maximum absorption wavelength (λ_{max}) of pyrazoline derivatives **3a**, **3b**, **3d** and **3e** in different solvents.

Compounds	$CHCl_3$ (nm)[a]	THF (nm)[a]	CH_3CN (nm)[a]
3a	336	334	329
3b	342	342	337
3d	336	337	332
3e	335	334	332

[a] Static dielectric constant of $CHCl_3$, THF and CH_3CN are 4.81, 7.52 and 36.64, respectively [J.A. Dean, Lange's Handbook of Chemistry, 15th ed., 1999].

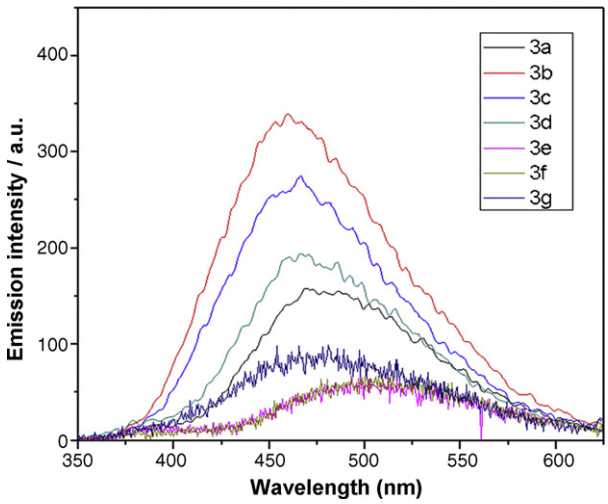


Fig. 6. Emission spectra of pyrazoline derivatives **3a–g** in chloroform solution with the concentration of 10^{-5} M.

Table 4
Maximum wavelength (nm) of excitement and emission of fluorescence of compounds **3a–g**.

	Name						
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
λ_{ex}	329	339	332	327	335	335	332
λ_{em}	470	459	466	466	512	513	481
Stokes shift	141	120	134	139	177	178	149

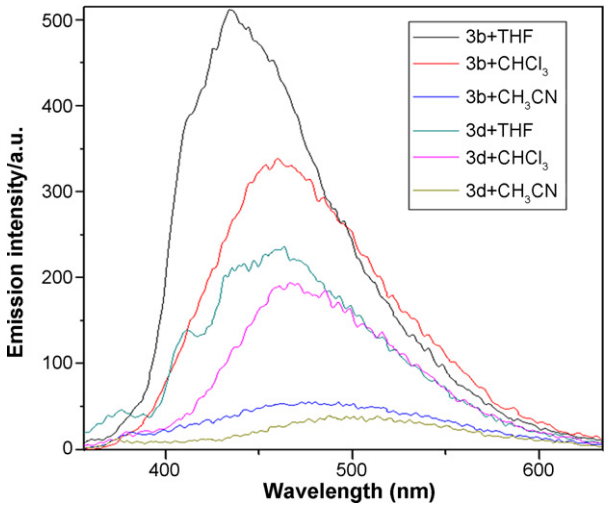


Fig. 7. Emission spectra of compounds **3b** and **3d** in different solution with the concentration of 10^{-5} M.

had also very strong influence on the emission of pyrazoline compounds. It can be observed that a strong electron-donating group in benzene ring such as methoxyl group on C3 position of pyrazoline made the emission wavelength of **3e**, **3f** and **3g** red shifted than that of compounds **3b**, **3c** and **3d** with chlorine group in benzene ring. Contrasting to it, the phenomenon is reversed to blue shift in the absorption spectrum. Therefore, Stokes shift relates with the attached substituent and it is enlarged when compound **3** possesses a strong electron-donating group in benzene ring. In the present study, the measured data are in agreement with the spectroscopic trends of similar, previously characterized 1,3,5-aryl-substituted pyrazolines in literature [34].

The solvent effects on the fluorescence characteristics of the compounds **3b** and **3d** were studied, which indicated that the emission wavelength of the compounds was red shifted and the fluorescence intensity was decreased with the increase in solvent polarity (Fig. 7). It is reported that the change of dipole moments between ground and excited state is primarily determined by *R*, which is therefore the major determinant for the magnitude of the solvatochromic shifts [34]. Bathochromic shift proves the π–π^* transition in the excited state. It is believed that the potential energy surface of the emitting state is different from that of the ground state and a photo-induced ICT takes place in the fluorescence states with increasing solvent polarity. That is to say that the molecule is solvated significantly in the S1 excited state, resulting in a difference in dipole moment between the S1 excited state and the ground state.

4. Conclusion

A series of novel 1,3,5-triaryl pyrazoline derivatives has been synthesized by the reaction of chalcone and 3-chloro-6-hydrazinylpyridazine in 47–82% yields. The structures of compounds obtained were determined by IR, ^{1}H NMR and HRMS spectra. Representatively, the spatial structure of compounds **3d** was determined by using X-ray diffraction analysis. The absorption maxima of the compounds vary from 332 to 342 nm depending on the group bonded to benzene rings. The maximum emission spectra of compounds in $CHCl_3$ are dependent on group in benzene ring in which a strong electron-donating group in benzene ring such as methoxyl group on C3 position of pyrazoline made the emission wavelength of **3e**, **3f** and **3g** red shifted than that of compounds **3b**, **3c** and **3d** with chlorine group. The intensity of absorption and fluorescence was also correlated with substituents on two aryl rings. In addition, the absorption spectra of these compounds change very little with increasing solvent polarity.

5. Supplementary materials

CCDC 746323 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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