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The synthesis, characterization and optical properties of novel, substituted, pyrazoly 1,3,4-oxadiazole derivatives

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ABSTRACT

A series of novel substituted pyrazoly 1,3,4-oxadiazole derivatives were synthesized by the reaction of substituted pyrazole-5-carbohydrazide with substituted benzoic acid in the presence of phosphorus oxychloride. The compounds were characterised using IR, ^{1}H NMR and HRMS and X-ray diffraction analysis. The absorption and fluorescence characteristics of the compounds were investigated in dichloromethane. The compounds displayed similar absorption, ranging from 267 to 281 nm with a strong absorption band occurring at ~275 nm. Correlation of the absorption spectra and fluorescence characteristics of the pyrazoly 1,3,4-oxadiazole derivatives with substituent effects on the benzene rings, revealed that a methoxy and a bromine group attached to the benzene ring markedly influenced maximum emission.

1. Introduction

1,3,4-Oxadiazole derivatives are highly attractive compounds for the development of materials for organic electroluminescent (EL) devices since these compounds possess high electron-accepting properties and display strong fluorescence with high quantum yield [1], as exemplified by 2,5-diphenyl-1,3,4-oxadiazole and 2,5-di-2-naphthyl-1,3,4-oxadiazole, for which quantum yields of 0.80 and 0.85 in cyclohexane solution, respectively, were reported [2]. Thus, compounds involving 1,3,4-oxadiazole rings have been used as electron-transporting materials and emitters in organic EL devices [3–5]. Recently, 1,3,4-oxadiazole derivatives have aroused considerable interests in the area of organic light-emitting diodes (OLEDs) [6–9].

Oxadiazole fragments have also been connected to classical chelating ligands (such as bipyridines) in luminescent complexes, to obtain multifunctional (emitting and charge transporting) molecular species [10–17]. Furthermore, substituted 1,3,4-oxadiazole derivatives also have been reported to show a broad spectrum of biological activity including anticancer effects [18,19]. In recent years, the application of 1,3,4-oxadiazoles consisting of five-membered heterocyclic have been described [20–24].

This paper concerns the design, synthesis, structural characterization and fluorescence properties of novel compounds with potential bioactivity in order to investigate the localization of small molecules in cells or the interaction of small molecules with proteins. This work describes the synthesis, characterization and optical properties of novel, substituted pyrazoly 1,3,4-oxadiazole derivatives.

2. Experimental

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. Synthesis

The synthetic approach for the preparation of substituted pyrazoly 1,3,4-oxadiazole derivatives is shown in Fig. 1. To a stirred

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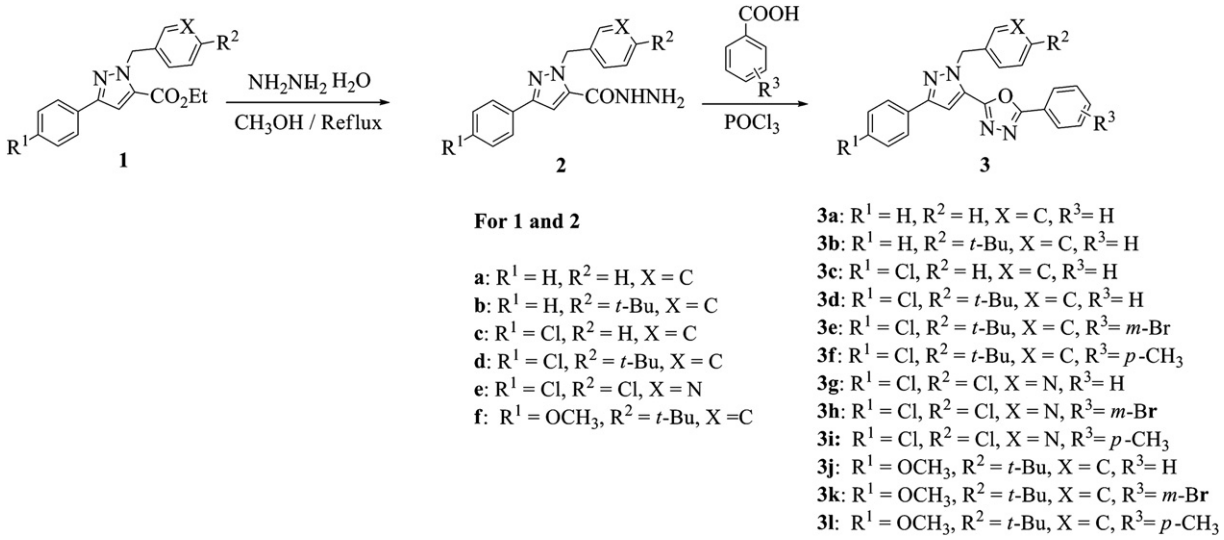

Fig. 1. Synthesis of substituted pyraxzoly 1,3,4-oxadiazole derivatives.

solution of compound **1** (1 mmol) in methanol (5 ml), 80% hydrazine monohydrate (1.2 ml) was added. The reaction mixture was maintained under reflux for 1–5 h, until TLC indicated the end of reaction. After this time, the reaction mixture was cooled to room temperature and left overnight, the ensuing solid material being was collected by filtration. The solid was recrystallized from ethanol to afford compound **2** in 72–93% yields. A solution of compound **2** (1 mmol) and substituted benzoic acid (1 mmol) in freshly distilled $POCl_3$ (caution: Reacts violently with water; incompatible with many metals, alcohols, amines, phenol, DMSO, strong bases) (5 ml) was refluxed for 6–12 h. Excess $POCl_3$ was distilled off and the residue was poured into iced water. The precipitate was filtered, washed with water, dried and recrystallized from ethanol to give compound **3** in 13–26%.

*2.2.1. 2-(1-Benzyl-3-phenyl-1H-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole (**3a**)*

Yield 18%, white solid, mp 164–166 °C; IR (KBr) ν/cm^{-1}: 1611 (C═C), 1547 (C═N), 1469 (N–N), 1256 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.00 (s, 2H, CH_2), 7.20–7.32 (m, 4H, ArH), 7.34–7.46 (m, 5H, ArH), 7.50–7.59 (m, 3H, ArH), 7.89 (d, J = 7.4 Hz, 2H, ArH), 8.10 (d, J = 7.9 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{24}H_{19}N_4O$: 379.1559; found: 379.1596.

*2.2.2. 2-(1-(4-Tert-butylbenzyl)-3-phenyl-1H-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole (**3b**)*

Yield 16%, white solid, mp 159–161 °C; IR (KBr) ν/cm^{-1}: 1615 (C═C), 1548 (C═N), 1473 (N–N), 1307 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 5.97 (s, 2H, CH_2), 7.25 (s, 1H, ArH), 7.28–7.40 (m, 5H, ArH), 7.44 (t, J = 7.5 Hz, 2H, ArH), 7.49–7.61 (m, 3H, ArH), 7.90 (d, J = 7.5 Hz, 2H, ArH), 8.10 (d, J = 6.9 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{28}H_{27}N_4O$: 435.2185; found: 435.2477.

*2.2.3. 2-(1-Benzyl-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole (**3c**)*

Yield 22%, white solid, mp 159–160 °C; IR (KBr) ν/cm^{-1}: 1611 (C═C), 1551 (C═N), 1473 (N–N), 1257 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.00 (s, 2H, CH_2), 7.23(s, 1H, ArH), 7.24–7.35 (m, 3H, ArH), 7.42 (d, J = 7.1 Hz, 4H, ArH), 7.50–7.63 (m, 3H, ArH), 7.83 (d, J = 8.0 Hz, 2H, ArH), 8.10 (d, J = 7.2 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{24}H_{18}ClN_4O$: 413.1169; found: 413.1163.

*2.2.4. 2-(1-(4-Tert-butylbenzyl)-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole (**3d**)*

Yield 18%, Yellow solid, mp 183–185 °C; IR (KBr) ν/cm^{-1}: 1614 (C═C), 1549 (C═N), 1448 (N–N), 1289 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 5.96 (s, 2H, CH_2), 7.22 (s, 1H, ArH), 7.30–7.44 (m, 6H, ArH), 7.51–7.61 (m, 3H, ArH), 7.83 (d, J = 8.3 Hz, 2H, ArH), 8.10 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{28}H_{26}ClN_4O$: 469.1795; found: 469.1787.

*2.2.5. 2-(3-Bromophenyl)-5-(1-(4-tert-butylbenzyl)-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-1,3,4-oxadiazole (**3e**)*

Yield 18%, white solid, mp 199–201 °C; IR (KBr) ν/cm^{-1}: 1613 (C═C), 1545 (C═N), 1470 (N–N), 1290 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 5.95 (s, 2H, CH_2), 7.23 (s, 1H, ArH), 7.32 (d, J = 8.5 Hz, 2H, ArH), 7.36 (d, J = 8.5 Hz, 2H, ArH), 7.39–7.44 (m, 3H, ArH), 7.70 (d, J = 8.3 Hz, 1H, ArH), 7.83 (d, J = 8.4 Hz, 2H, ArH), 8.05 (d, J = 8.0 Hz, 1H, ArH), 8.23 (t, J = 1.6 Hz, 1H, ArH); HRMS calcd for $[M + H]^+$ $C_{28}H_{25}BrClN_4O$: 547.0900; found: 547.0898.

*2.2.6. 2-(1-(4-Tert-butylbenzyl)-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-5-p-tolyl-1,3,4-oxadiazole (**3f**)*

Yield 19%, yellow solid, mp 149–151 °C; IR (KBr) ν/cm^{-1}: 1612 (C═C), 1555 (C═N), 1472 (N–N), 1289 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 2.45 (s, 3H, CH_3), 5.96 (s, 2H, CH_2), 7.20 (s, 1H, ArH), 7.31 (d, J = 8.3 Hz, 2H, ArH), 7.34 (d, J = 8.4 Hz, 2H, ArH), 7.37 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8.5 Hz, 2H, ArH), 7.82 (d, J = 8.5 Hz, 2H, ArH), 7.99 (d, J = 8.3 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{29}H_{28}ClN_4O$: 483.1952; found: 483.1934.

*2.2.7. 2-(3-(4-Chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1H-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole (**3g**)*

Yield 14%, white solid, mp 200–201 °C; IR (KBr) ν/cm^{-1}: 1617 (C═C), 1553 (C═N), 1472 (N–N), 1289 (C–O–C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.00 (s, 2H, CH_2), 7.23 (s, 1H, ArH), 7.27 (d, J = 8.7 Hz, 1H, ArH), 7.43 (d, J = 8.7 Hz, 2H, ArH), 7.52–7.66 (m, 3H, ArH), 7.80 (d, J = 8.4 Hz, 1H, ArH), 7.81 (d, J = 8.4 Hz, 2H, ArH), 8.12 (d, J = 8.1 Hz, 2H, ArH), 8.56 (d, J = 2.1 Hz, 1H, ArH); HRMS calcd for $[M + H]^+$ $C_{23}H_{16}Cl_2N_5O$: 448.0732; found: 448.0733.

*2.2.8. 2-(3-Bromophenyl)-5-(3-(4-chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1H-pyrazol-5-yl)-1,3,4-oxadiazole (**3h**)*

Yield 19%, white solid, mp 228–230 °C; IR (KBr) ν/cm^{-1}: 1617 (C=C), 1567 (C=N), 1463 (N–N), 1306 (C–O–C); H NMR (400 MHz, $CDCl_3$) δ: H NMR (400 MHz, $CDCl_3$) δ: 6.00 (s, 2H, CH_2), 7.25 (s, 1H, ArH), 7.27 (d, J = 8.0 Hz, 1H, ArH), 7.43 (d, J = 8.6 Hz, 2H, ArH), 7.45 (d, J = 8.0 Hz, 1H, ArH), 7.73 (d, J = 7.8 Hz, 1H, ArH), 7.80 (t, J = 7.8 Hz, 1H, ArH), 7.81 (d, J = 8.6 Hz, 2H, ArH), 8.08 (d, J = 7.8 Hz, 1H, ArH), 8.25 (t, J = 1.6 Hz, 1H, ArH), 8.55 (d, J = 2.3 Hz, 1H, ArH); HRMS calcd for $[M + H]^+$ $C_{23}H_{15}BrCl_2N_5O$: 525.9837; found: 525.9847.

*2.2.9. 2-(3-(4-Chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1H-pyrazol-5-yl)-5-p-tolyl-1,3,4-oxadiazole (**3i**)*

Yield 13%, white solid, mp 199–201 °C; IR (KBr) ν/cm^{-1}: 1613 (C=C), 1552 (C=N), 1470 (N–N), 1290 (C–O–C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.46 (s, 3H, CH_3), 5.99 (s, 2H, CH_2), 7.22 (s, 1H, ArH), 7.27 (d, J = 8.1 Hz, 1H, ArH), 7.36 (d, J = 7.8 Hz, 2H, ArH), 7.42 (d, J = 8.7 Hz, 2H, ArH), 7.79 (d, J = 8.7 Hz, 1H, ArH), 7.80 (d, J = 8.4 Hz, 2H, ArH), 8.00 (d, J = 8.1 Hz, 2H, ArH), 8.55 (d, J = 2.1 Hz, 1H, ArH); HRMS calcd for $[M + H]^+$ $C_{24}H_{18}Cl_2N_5O$: 462.0888; found: 462.0898.

*2.2.10. 2-(1-(4-Tert-butylbenzyl)-3-(4-methoxyphenyl)-1H-pyrazol-5-yl)-5-phenyl-1,3,4-oxadiazole (**3j**)*

Yield 26%, white solid, mp 176–178 °C; IR (KBr) ν/cm^{-1}: 1614 (C=C), 1549 (C=N), 1481 (N–N), 1251 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 3.86 (s, 3H, OCH_3), 5.95 (s, 2H, CH_2), 6.97 (d, J = 7.9 Hz, 2H, ArH), 7.17 (s, 1H, ArH), 7.30 (d, J = 7.3 Hz, 2H, ArH), 7.36 (d, J = 7.3 Hz, 2H, ArH), 7.47–7.62 (m, 3H, ArH), 7.82 (d, J = 7.9 Hz, 2H, ArH), 8.10 (d, J = 6.4 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{29}H_{29}N_4O_2$: 465.2291; found: 465.2286.

*2.2.11. 2-(3-Bromophenyl)-5-(1-(4-tert-butylbenzyl)-3-(4-methoxyphenyl)-1H-pyrazol-5-yl)-1,3,4-oxadiazole (**3k**)*

Yield 14%, yellow solid, mp 175–177 °C; IR (KBr) ν/cm^{-1}: 1611 (C=C), 1544 (C=N), 1478 (N–N), 1288 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 3.86 (s, 3H, OCH_3), 5.95 (s, 2H, CH_2), 6.98 (d, J = 8.7 Hz, 2H, ArH), 7.19 (s, 1H, ArH), 7.31 (d, J = 8.5 Hz, 2H, ArH), 7.35 (d, J = 8.5 Hz, 2H, ArH), 7.42 (t, J = 7.9 Hz, 1H, ArH), 7.70 (d, J = 7.9 Hz, 1H, ArH), 7.83 (d, J = 8.7 Hz, 2H, ArH), 8.05 (d, J = 7.9 Hz, 1H, ArH), 8.23 (s, 1H, ArH); HRMS calcd for $[M + H]^+$ $C_{29}H_{28}BrN_4O_2$: 543.1396; found: 543.1399.

*2.2.12. 2-(1-(4-Tert-butylbenzyl)-3-(4-methoxyphenyl)-1H-pyrazol-5-yl)-5-p-tolyl-1,3,4-oxadiazole (**3l**)*

Yield 14%, yellow solid, mp 169–171 °C; IR (KBr) ν/cm^{-1}: 1613 (C=C), 1555 (C=N), 1480 (N–N), 1288 (C–O–C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 9H, CH_3), 2.44 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 5.94 (s, 2H, CH_2), 6.97 (d, J = 8.7 Hz, 2H, ArH), 7.15 (s, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.32 (d, J = 8.6 Hz, 2H, ArH), 7.35 (d, J = 8.4 Hz, 2H, ArH), 7.81 (d, J = 8.7 Hz, 2H, ArH), 7.98 (d, J = 8.6 Hz, 2H, ArH); HRMS calcd for $[M + H]^+$ $C_{30}H_{31}N_4O_2$: 479.2447; found: 479.2689.

2.3. X-ray crystallography

Crystals of compounds **3e** and **3f** suitable for X-ray diffraction were obtained by slow evaporation of a solution of the solid in ethyl acetate at room temperature for 7 days, respectively. The crystals with approximate dimensions of 0.16 mm × 0.15 mm × 0.12 mm for **3e** and 0.18 mm × 0.15 mm × 0.12 mm for **3f** were mounted on a Bruker Smart Apex II CCD equipped with a graphite monochromated MoKα radiation (λ = 0.71073 Å) by using ϕ and ω scan modes and the data were collected at 293(2) K. The structures of the two crystals were solved by direct methods and refined by full-matrix least-squares techniques implemented in the SHELXTL-97 crystallographic software. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to carbon were located by geometrical calculations, with their position and thermal parameters being fixed during the structure refinement. The final refinement converged at R^1 = 0.0721, wR^2 = 0.1954 for **3e** and R^1 = 0.0601, wR^2 = 0.1261 for **3f**.

3. Results and discussion

3.1. Synthesis

The compound **1** reacted with hydrazine hydrate to afford compound **2** in good yield according to our previous reported method [25]. The reaction of compound **2** and substituted benzoic acid in the presence of phosphorus oxychloride gave desired compound **3**. After work-up and the recrystallization from suitable solvent pure products were obtained although the yields were lower.

3.2. Structure characterization

The assumed structures of compounds **3a**–**l** were proved by IR, ^{1}H NMR and HRMS spectra. For example compound **3f**, obtained as yellow crystal, gave a [M + H]-ion peak at *m/z* 483.1934 in the

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

	3e	**3f**
Empirical formula	$C_{28}H_{24}BrClN_4O$	$C_{29}H_{27}ClN_4O$
Formula weight	547.87	483.00
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/*n*	P– 1
Unit cell dimensions	a = 8.405(3) Å, α = 90° b = 15.874(6) Å, β = 96.35(8)° c = 19.656(8) Å, γ = 90°	a = 10.8995(15) Å, α = 74.050(3)° b = 10.9450(14) Å, β = 85.09(3)° c = 12.2368(16) Å, γ = 65.13(2)°
Volume	2606.4(18) A^3	1272.7(3) A^3
Z	4	2
Calculated density	1.396 Mg/m^3	1.260 Mg/m^3
Absorption coefficient	1.70 mm^{-1}	0.18 mm^{-1}
F(000)	1120	508
Crystal size	0.16 × 0.15 × 0.12 mm	0.18 × 0.15 × 0.12 mm
θ range for data collection	1.65–25.05°	1.73–25.05°
Limiting indices	$-9 \le h \le 9$, $-18 \le k \le 17$, $-18 \le l \le 23$	$-12 \le h \le 12$, $-9 \le k \le 13$, $-12 \le l \le 14$
Reflections collected/ unique	13 128/4587 [R(int) = 0.079]	6797/4481 [R(int) = 0.033]
Completeness to θ = 25.05°	99.4%	99.5
Absorption correction	None	None
Max. and min. transmission	0.8213 and 0.772	0.9788 and 0.9685
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	4587/570/317	4481/147/351
Goodness-of-fit on F^2	1.024	1.001
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0721, wR_2 = 0.1954	R_1 = 0.0601, wR_2 = 0.1261
R indices (all data)	R_1 = 0.1480, wR_2 = 0.2523	R_1 = 0.1414, wR_2 = 0.1689
Largest diff. peak and hole	0.526 and −0.573 e. Å^{-3}	0.197 and −0.199 e. Å^{-3}

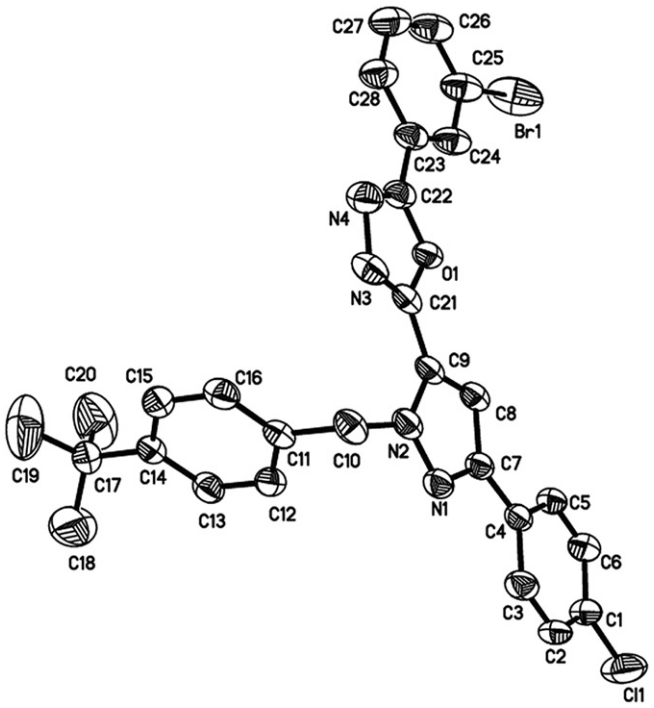

Fig. 2. The molecular structure of compound **3e**, with displacement ellipsoids drawn at the 50% probability level and H atoms omitted.

HRESIMS, in accord with the molecular formula $C_{29}H_{28}ClN_4O$. The IR spectra of compound **3f** showed the characteristic absorption bands at 1612 (C═C), 1555 (C═N), 1472 (N–N), 1289 (C–O–C). The ^{1}H NMR spectra ($CDCl_3$) of compound **3f** revealed four singlet peaks at δ 1.26 (9H, 3 × CH_3), 2.45 (3H, CH_3), 5.96 (2H, CH_2), and 7.20 (1H, pyrazole moiety) which were readily assigned to the hydrogen of tert-butyl, methyl, methylene and pyrazole moiety, respectively. Moreover, compound **3f** showed six doublet peaks at δ 7.31 (2H, J = 8.3 Hz), 7.34 (2H, J = 8.4 Hz), 7.37 (2H, J = 8.4 Hz), 7.41 (2H, J = 8.5 Hz), 7.82 (2H, J = 8.5 Hz), 7.99 (2H, J = 8.3 Hz) assigned to the protons on the three benzene ring, respectively. All other signals are consistent with the structure of **3f**.

3.3. Crystal structure

The spatial structures of compounds **3e** and **3f** were determined by using X-ray diffraction analysis. A summary of crystallographic data collection parameters and refinement parameters for **3e** and **3f** are compiled in Table 1.

The single crystal structure and atomic numbering chosen for **3e** are shown in Fig. 2. The C–C distances of phenyl ring (C11–16) are quasi equal and close to 1.38 Å except C11–C12 (1.391 Å) and C11–C16 (1.366 Å), this may be because the interaction between the pyrazole ring and the C11 atom through C10 atom. The C–C distances of C4 phenyl ring are quasi equal except C3–C4 and C4–C5 and this is because the strong interaction between the pyrazole ring and the C4 atom makes the C4 atom close to the pyrazole ring. The C–C distances of C23 phenyl ring vary from 1.351 Å to 1.407 Å. The bond length C9–C21 (1.449 Å) is similar to *N*, *N*-Dimethyl-4-[5-(5-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1,3,4-oxadiazol-2-yl]aniline(C8–C11 1.443 Å) [26]. The dihedral angles between the pyrazole ring and the C4 phenyl or 1,3,4-oxadiazole ring are 6.72° and 8.61°, respectively. The dihedral angle between the 1,3,4-oxadiazole ring and the C23 phenyl ring is 5.78°. All the dihedral angles above are so small that the four rings in **3e** is nearly in the same plane and this coplanar conformation provides a large conjugated system which makes transporting of electrons easy. In contrast, the dihedral angle between pyrazole ring and the C11

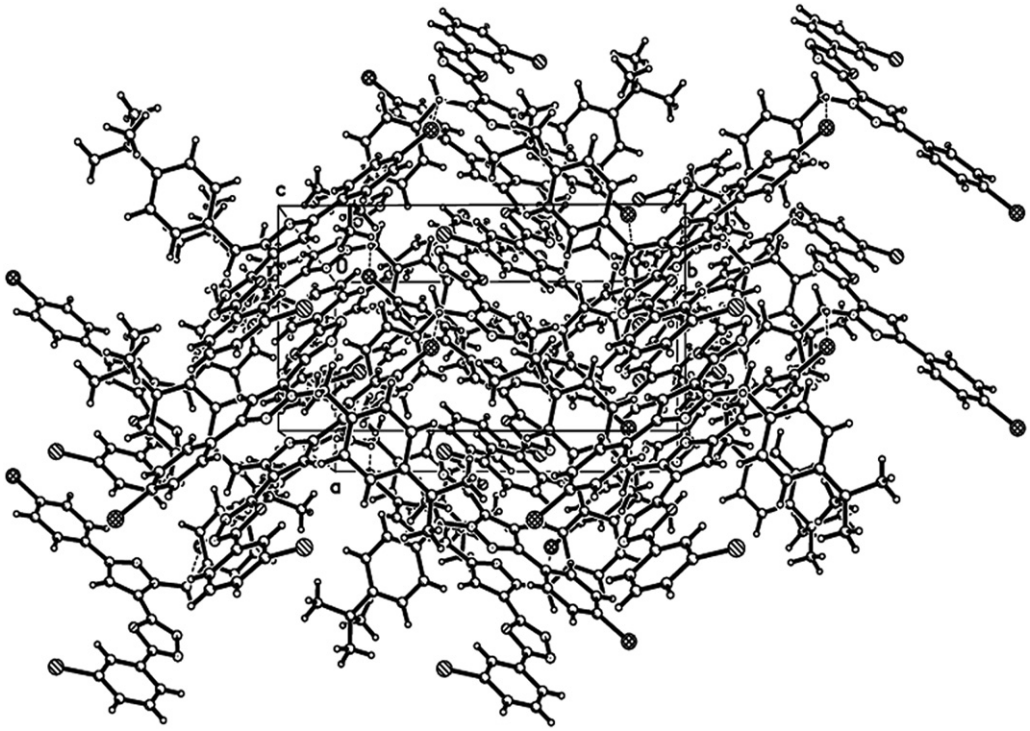

Fig. 3. The crystal packing of compound **3e**.

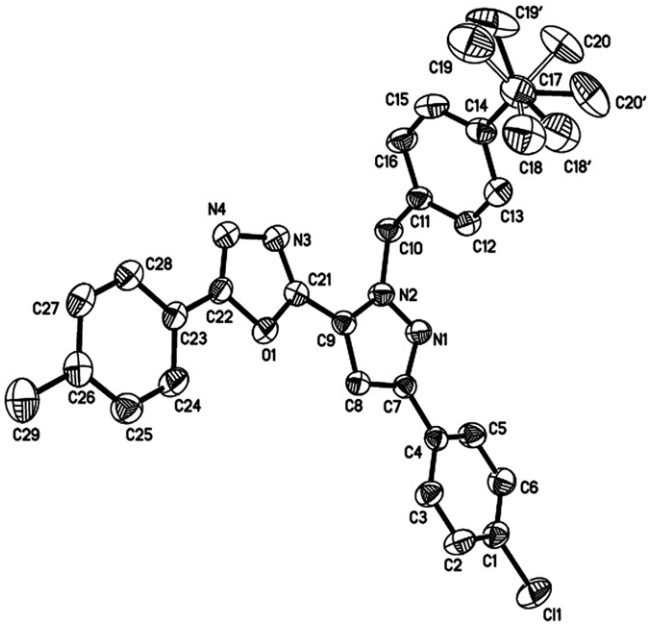

Fig. 4. The molecular structure of compound **3f**, with displacement ellipsoids drawn at the 50% probability level and H atoms omitted.

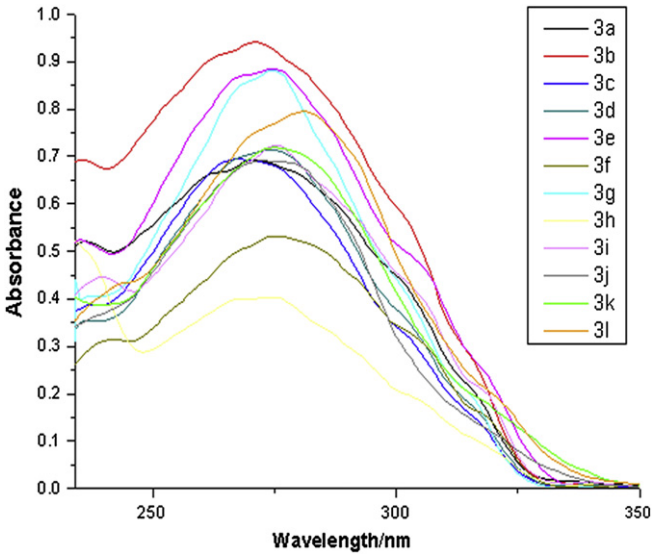

Fig. 6. The UV–vis spectra of the compounds **3a**–**l** in dichloromethane (2×10^{-5} M).

phenyl ring is 80.71 and it means that C11 phenyl ring does not participate in conjugation system. The crystal packing of **3e** is illustrated in Fig. 3.

The single crystal structure and atomic numbering chosen for **3f** are shown in Fig. 4 and the packing structure of **3f** is illustrated in Fig. 5. The C–C distances and the dihedral angles in **3f** are very similar to **3e**. It would be mentioned that the tert-butyl group exhibits rotational disorder between two orientations in a 0.61:0.39 ratio in **3f**.

3.4. Absorption spectral characteristics of the compounds *3a–l*

The UV–vis spectra of the compounds **3a**–**l** measured in dichloromethane solutions are shown in Fig. 6 and the optical characteristics are summarized in Table 2. As shown in Fig. 6 compounds **3a**–**l** display similar absorptions ranging from 267 to 281 nm that are attributed to π–π^* transition of conjugate system and the strong absorption band at about 275 nm (Table 2). It is noticed that the substituent has definite effects on the absorption bands although it is small. The maximum absorption of compound **3c** with electron-withdrawing groups (Cl) result in a blue shift (4 nm) contrasting compound **3a**. Similarly, comparing compound

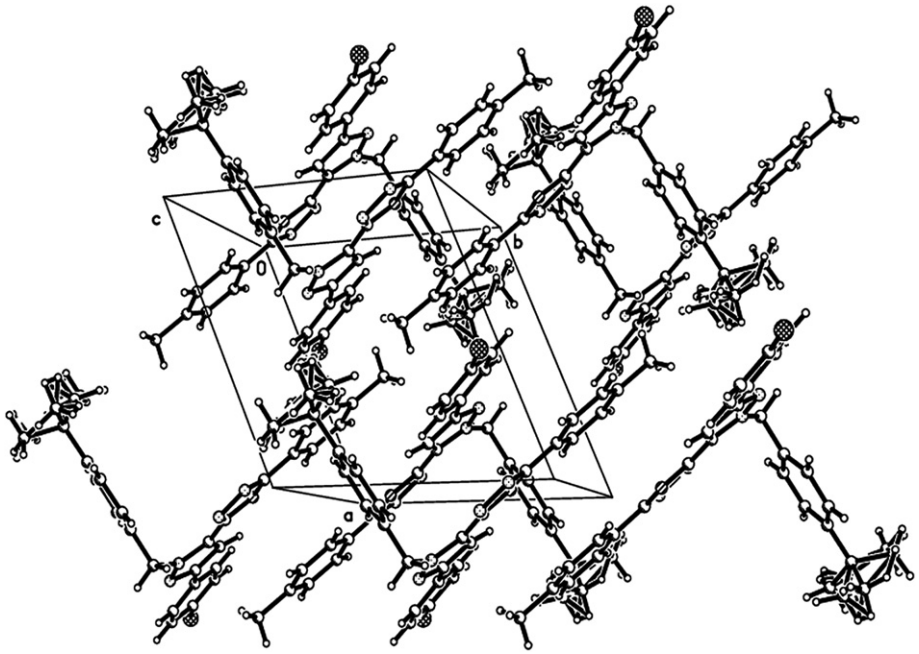

Fig. 5. The crystal packing of compound **3f**.

Table 2
The optical characteristics of the compounds **3a**–**l** in dichloromethane.

Compound	λ_{max} (nm)	λ_{ex} (nm)	ε_{max} (mol^{-1} cm^{-1})	F_{max} (nm)	Stokes shift (nm)
3a	271	278	34 665	369	91
3b	271	276	47 060	366	90
3c	267	280	34 755	364	84
3d	274	280	35 685	360	80
3e	274	280	44 175	375	95
3f	275	286	26 585	362	76
3g	275	275	44 020	360	85
3h	274	277	20 180	372	95
3i	275	277	38 635	356	79
3j	273	281	34 560	406	125
3k	275	280	35 935	422	147
3l	281	290	39 725	401	120

3f and **3l**, electron-withdrawing groups (Cl) result in a blue shift (6 nm) with contrast to an electron-donating group (MeO). Compounds **3d**–**i** have almost same maximum absorption (274–275 nm) that means substituent R^2 and R^3 do not influence the absorption.

3.5. Fluorescence spectral characteristics

Fig. 7 presents the emission spectra of compounds **3a**–**l** in dichloromethane solution (2×10^{-6} M). Their excitation wavelengths are shown in Table 2. It can be found that their intensity of fluorescence and maximal emission bands are dependent on the groups bonded to benzene rings. Maximal emission bands of compounds **3a**–**l** display ranging from 356 to 422 nm. Maximal emission bands of **3e**, **3h** and **3k**, in which bromine bonded to benzene ring, are red-shifted 13, 16 and 21 nm, respectively, comparing to **3f**, **3i** and **3l**, in which methyl group bonded to benzene ring. Moreover, maximal emission wavelength of **3k** is red-shifted 47 nm comparing to **3e** due to the effect of methoxyl group in benzene ring; similarly, maximal emission wavelength of **3l** is red-shifted 39 nm comparing to **3f**. Stocks shift of compounds **3a**–**l** are also dependent on the groups bonded to benzene rings in a similar manner. Taken together, methoxyl group and bromine bonded to benzene ring influence maximal emission bands much more.

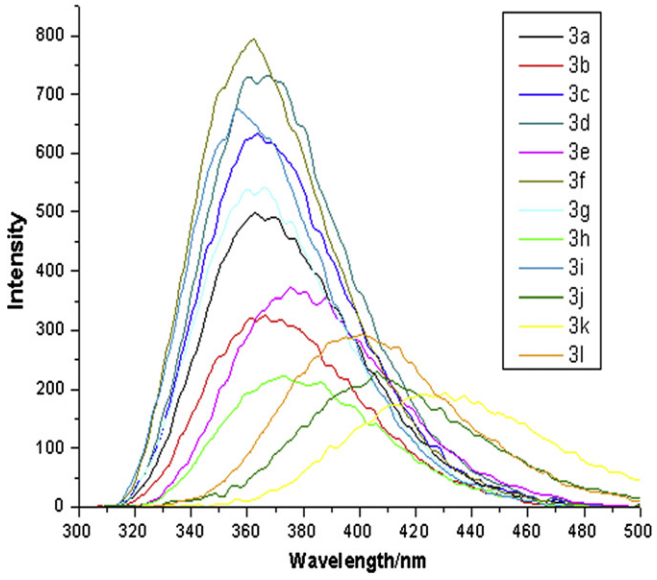

Fig. 7. The Fluorescence spectra of the compounds **3a**–**l** in dichloromethane (2×10^{-6} M).

4. Conclusion

A series of novel substituted pyrazoly 1,3,4-oxadiazole derivatives has been synthesized by the reaction of substituted pyrazole-5-carbohydrazide with substituted benzoic acid in the presence of phosphorus oxychloride. The structures of compounds obtained were determined by IR, ^{1}H NMR and HRMS spectra, typically, the spatial structures of compounds **3e** and **3f** were determined by using X-ray diffraction analysis. Absorption and fluorescence spectral characteristics of the compounds were investigated in dichloromethane by UV–vis absorption and emission spectra. The absorption spectra and fluorescence characteristics were correlated with substituent on benzene rings.

5. Supplementary materials

CCDC 752716 and 752717 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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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