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Synthesis, spectroscopic characterisation and X-ray analysis of regioisomeric 1,3,5-trisubstituted pyrazoles

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ABSTRACT

A new series of regioisomeric 1,3,5-trisubstituted pyrazoles **7–9(a,b)** have been synthesized by the reaction of β-diketones (**4–6**) with methyl hydrazine in ethanol. All the compounds are characterised by the FT-IR, ^{1}H, ^{13}C NMR and mass spectrometry. The crystal structure of compounds **7a, 7b** and minor isomer **8b** have been determined by X-ray single crystal analysis which showed either of the substituted groups attached to pyrazole ring are essentially non-planar to the central pyrazole ring. Addition of trace amounts of acetic acid during the synthesis of compound **8** resulted in an unexpected compound **10** which is characterised by the X-ray single crystal analysis and is essentially planar. However, crystal structure of **10** is already reported. All structures are further stabilized by the classic and non-classic inter- and intramolecular hydrogen bonding.

1. Introduction

Pyrazole and its derivatives have wide applications in the pharmaceutical and agrochemical industries [1]. A number of substituted pyrazoles exhibit HIV-1 reverse transcriptase and IL-1 synthesis inhibition as well as bacteriostatic, fungicidal, bactericidal, antipyretic and analgesic activity [2–5]. Many heterocyclic compounds such as pyrazoles, imidazoles and triazoles are known to possess anti-fertility properties [6]. Some pyrazole derivatives have been reported to have moderate anti-malarial activities [7] and are also used as anti-inflammatory [8,9] anti-hyperglycaemic [10] multidrug resistance modulating (MRD) [11] and analgesic agents [12].

Some pyrazole derivatives have also been used as energetic compounds because they have high formation enthalpy, good thermal stability and safety characteristics. They are used in energetic formulations as oxidizers, plasticizer and elastomeric binders [13].

Pyrazole compounds are widely used as an extraction reagent in the separation of trace metals [14]. Transition metal complexes of pyrazoles and there derivatives have widely shown herbicidal, fungicidal [15] and anti-amoebic activity [16]. Coordination of pyrazole and its derivatives to the metal centre of various biologically active molecules modifies their activity. Pyrazoles are used as building blocks in heterocyclic synthesis, as optical brighteners and UV-stabilizers [17].

The synthesis of pyrazoles and their derivatives has been well explored using the so-called [3 + 2] atom fragments, where β-diketones are used as 3-atom building blocks and hydrazines as the 2-atom fragment [18]. In view of wide synthetic and biological applications of the pyrazole compounds, we have synthesized and structurally characterised six new pyrazole derivatives (Fig. 1). The X-ray structures of compound **7a**, **7b, 8b** and **10** are also reported herein.

2. Experimental

2.1. Chemicals and instrumentation

All the chemicals used in the synthesis were of analytical grade and used without further purification. All the solvents were dried before use by the literature methods [19].

Melting points were determined on a Barnstead Electrothermal (UK) 9200 and are uncorrected. The infrared spectra were recorded on FT-IR-8400S shimadzu spectrometer as KBr pellets. The ^{1}H NMR and ^{13}C NMR were run on Bruker 300 MHz and 75 MHz NMR spectrometer respectively in DMSO-d_6, using TMS as an internal standard. Low resolution mass spectra were obtained on Finnigan MAT 312.

2.2. Synthesis

The β-diketones **4–6** were prepared by the already reported procedure [20,21].

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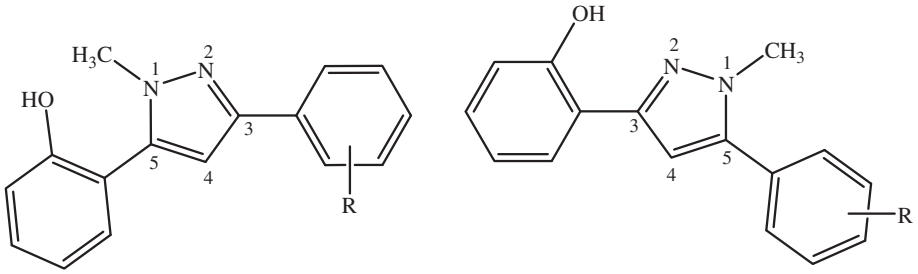


Fig. 1. General structure and numbering scheme of synthesized regioisomeric pyrazoles.

2.2.1. General procedure for the preparation of 1,3,5-trisubstituted pyrazoles (7/9 a,b)

0.5 mol of β-diketone (**4,6**) was dissolved in ethanol (130 mL) in a round bottom flask fitted with a reflux condenser. When all the β-diketone was dissolved, 0.5 mol of methyl hydrazine was added drop wise. After the addition of methyl hydrazine, the reaction mixture was refluxed for 6 h. The major isomer **7/9** was separated as soon as formed as fine crystals which was filtered and recrystallized from ethanol. The filtrate was concentrated and the crude solid was purified by column chromatography, which gave the minor isomer **7/9b**, which was recrystallized from ethanol.

2.2.1.1. 1-Methyl-5-(2′-hydroxyphenyl)-3-phenylpyrazole (7a). Yield 53%; m.p. 163–165 °C; R_f value 0.13 (1,2-dichloroethane); FT-IR (KBr cm^{-1}) 3605 (OH), 1629 (C=N); 1615 (C=C), 1364 (C—N); ^{1}H NMR (DMSO, δ ppm) 9.95 (s, 1H, Ar—OH), 7.33–6.91 (m, 9H, Ar—H), 6.69 (s, 1H, pyrazole-H4); 3.72 (s, 3H, NCH_3): ^{13}C NMR (DMSO, δ ppm) 155.02, 148.78, 142.07, 133.57, 131.28, 130.38, 128.59 (2C), 127.21, 124.93 (2C), 119.16, 117.39, 115.96, 103.66, 37.22; MS m/z (%) 250.2 (M^+, 100), 224 (30), 205 (20), 178 (35), 153 (13), 118 (75), 91 (5), 77 (25), 51 (9).

2.2.1.2. 1-Methyl-3-(2′-hydroxyphenyl)-5-phenylpyrazole (7b). Yield 17.4%; m.p. 98–100 °C; R_f value 0.69 (1,2-dichloroethane); FT-IR (KBr cm^{-1}) 3620 (OH), 1630 (C=N), 1610 (C=C), 1370 (C—N); ^{1}H NMR (DMSO, δ ppm) 10.88 (s, 1H, Ar—OH), 7.58–6.91 (m, 9H, Ar—H), 6.65 (s, 1H, pyrazole-H4), 3.88 (s, 3H, NCH_3): ^{13}C NMR (DMSO, δ ppm) 155.92, 150.31, 144.61, 129.86, 128.98, 128.89, 128.75 (2C), 127.93, 126.14, 119.17, 116.97, 116.53, 102.42, 37.38; MS m/z (%) 250.4 (M^+, 100), 222.3 (23), 207.3 (23), 178 (30), 152 (13), 118.2 (70), 91.1 (10), 77.1 (23), 51 (8).

2.2.1.3. 1-Methyl-5-(2′-hydroxyphenyl)-3-(4″-methoxyphenyl)pyrazole (9a). Yield 54%; m.p. 160–162 °C; R_f value 0.11 (1,2-dichloroethane); FT-IR (KBr cm^{-1}) 3620 (OH), 1640 (C=N), 1607 (C=C), 1365 (C—N), 1250 (OCH_3); ^{1}H NMR (DMSO, δ ppm) 9.89 (s, 1H, Ar—OH), 7.74–6.69 (m, 8H, Ar—H), 6.58 (s, 1H, pyrazole-H4), 3.76 (s, 3H, OCH_3), 3.69 (s, 3H, NCH_3); ^{13}C NMR (DMSO, δ ppm) 158.63, 154.95, 148.67, 141.88, 131.21 (2C), 130.24, 126.29, 126.18, 119.10, 117.48, 115.93, 113.97, 103.02, 54.01, 37.05; MS m/z (%) 280 (M^+, 100), 237 (21), 193.9 (6), 165 (24), 146 (14), 139 (11), 118 (12), 77 (27), 63 (33).

2.2.1.4. 1-Methyl-3-(2′-hydroxyphenyl)-5-(4″-methoxyphenyl)pyrazole (9b). Yield 7%; m.p. 95–97 °C; R_f value 0.81 (1,2-dichloroethane); FT-IR (KBr cm^{-1}) 3610 (OH), 1640 (C=N), 1600 (C=C), 1364 (C—N), 1230 (OCH_3); ^{1}H NMR (DMSO, δ ppm) 10.88 (s, 1H, Ar—OH), 7.56–6.86 (m, 8H, Ar—H), 6.59 (s, 1H, pyrazole-H4), 3.85 (s, 3H, OCH_3), 3.58 (s, 3H, NCH_3); ^{13}C NMR (DMSO, δ ppm) 160.10, 155.95, 150.27, 144.46, 130.09 (2C), 128.93, 126.13, 122.19, 119.15, 116.97, 116.64, 114.23 (2C), 102.10, 55.35, 37.32; MS m/z (%) 280 (M^+, 100), 265 (46), 252 (10), 237 (12), 165 (17), 148 (55), 140 (32), 118 (9), 77 (6).

2.2.2. Preparation of 1,3,5 –trisubstituted pyrazoles (8a,b)

0.5 mol of β-diketone **5** was dissolved in ethanol (130 mL) in a round bottom flask fitted with a reflux condenser and 3 mL of glacial acetic acid was added. When the whole β-diketone was dis-

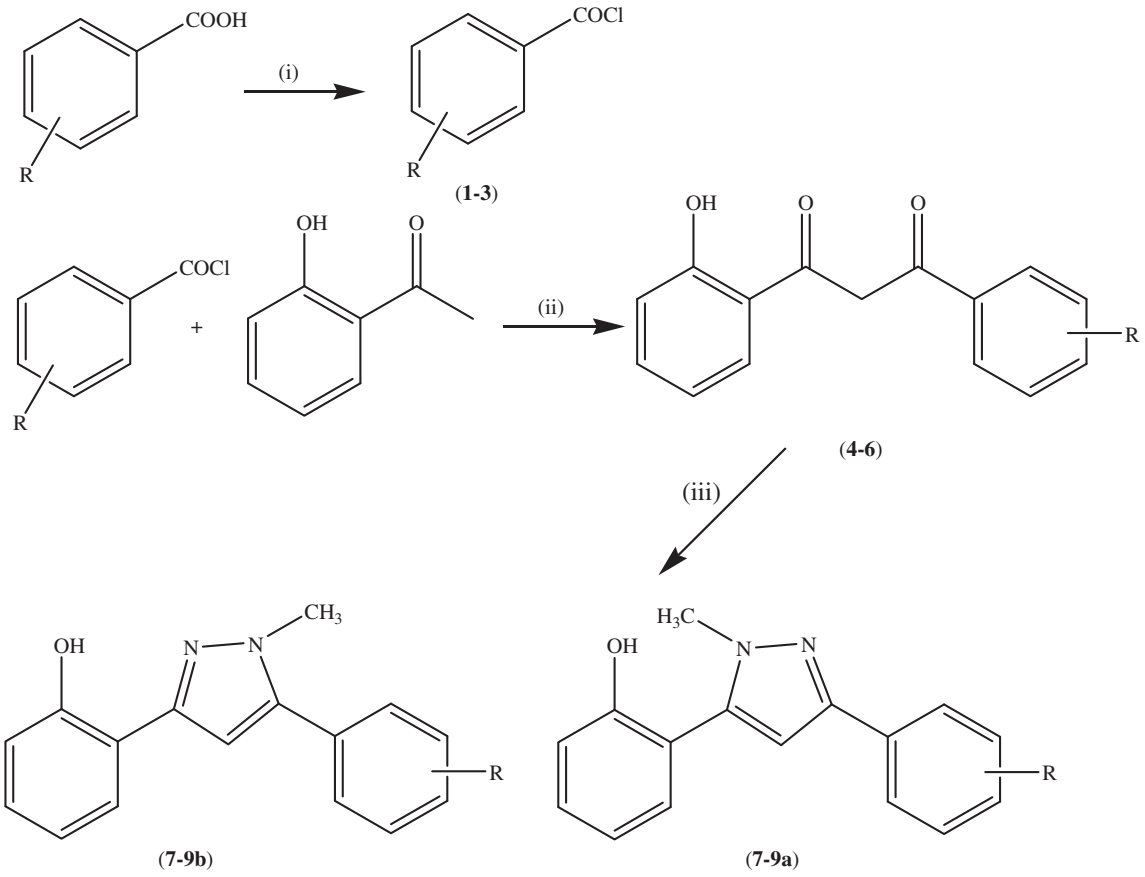
Table 1
Crystal data and structure refinements for compounds **7a, 7b, 8b** and **10.**

	Compound **7a**	Compound **7b**	Compound **8b**	Compound **10** [25]
Empirical formula	$C_{16}H_{14}N_2O$	$C_{16}H_{14}N_2O$	$C_{17}H_{16}N_2O_2$	$C_{16}H_{14}N_2O_2$
Formula weight	250.29	250.29	280.32	266.29
Crystal shape (colour)	Block (yellow)	Block (colourless)	Block (colourless)	Block (yellow)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	P·21·21·21	P·21/c	P·21/n	P·2c–2n
Unit cell dimension				
a (Å)	4.6677(4)	10.3020(8)	10.4877(7)	17.5093(16)
b (Å)	12.3866(10)	6.9323(6)	12.4162(8)	10.1881(9)
c (Å)	21.6888(18)	18.6692(15)	11.4276(8)	7.4386(7)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.00	100.2200(10)	96.9640(10)	90.00
γ (°)	90.00	90.00	90.00	90.00
V (Å ^{3})	1253.98(18)	1312.14(19)	1477.09(17)	1326.9(2)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.326	1.267	1.261	1.333
Crystal size (mm)	0.32 × 0.28 × 0.25	0.32 × 0.28 × 0.24	0.28 × 0.26 × 0.24	0.32 × 0.26 × 0.25
F(0 0 0)	528	528	592	560
Total reflections	1812	3170	3602	1735
Goodness-of-fit	1.069	0.990	1.026	1.071
θ Range for data collection (°)	2.50–28.28	2.72–28.28	2.43–28.33	3.07–28.25

solved, 0.5 mol of methyl hydrazine was added drop by drop. After addition the of methyl hydrazine the reaction mixture was refluxed till the completion of the reaction. The major isomer **8a** separated as soon as formed as fine crystals which was filtered and recrystallized from ethanol. The filtrate was concentrated and the crude solid was purified by column chromatography, which gave the minor isomer **8b**, which was recrystallized from ethanol and an unexpected product **10**, which was characterised by X-ray crystallography.

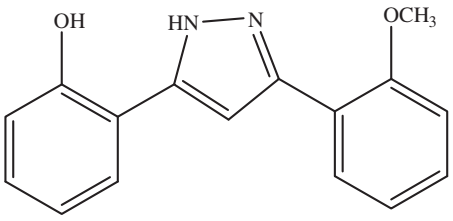
2.2.2.1. 1-Methyl-5-(2′-hydroxyphenyl)-3-(2″-methoxyphenyl)pyrazole (8a). Yield 54%; m.p. 214–216 °C; R_f value 0.11 (1, 2-dichloroethane); FT-IR (KBr cm^{-1}) 2939 (OH), 1628 (C=N), 1607 (C=C), 1360 (C—N), 1246 (OCH_3); ^1H NMR (DMSO-d_6, δ ppm) 9.97 (s, 1H, Ar—OH), 7.96–6.89 (m, 8H, Ar—H), 6.67 (s, 1H, pyrazole-H4), 3.84 (s, 3H, OCH_3), 3.75 (s, 3H, NCH_3); ^{13}C NMR (DMSO, δ ppm), 156.39, 155.08, 145.73, 141.05, 131.36, 130.32, 128.48, 127.60, 122.12, 120.52, 119.24, 117.68, 116.05, 111.85, 107.72, 55.36, 37.19; MS m/z (%) 280.2 (M^+, 100), 248 (35), 165 (12), 118 (20), 77 (6).

2.2.2.2. 1-Methyl-3-(2′-hydroxyphenyl)-5-(2″-methoxyphenyl)pyrazole (8b). Yield 10%; m.p. 77–79 °C; R_f value 0.77 (1, 2-dichloroethane); FT-IR (KBr cm^{-1}) 2934 (OH), 1630 (C=N), 1600 (C=C), 1362 (C—N), 1248 (OCH_3); ^1H NMR (DMSO, δ ppm) 10.94 (s, 1H, Ar—OH), 7.57–6.88 (m, 8H, Ar—H), 6.59 (s, 1H, pyrazole-H4), 3.83 (s, 3H, OCH_3), 3.74 (s, 3H, NCH_3); ^{13}C NMR (DMSO, δ ppm); 156.98, 155.90, 150.14, 141.46, 131.63, 130.95, 128.76, 126.12, 120.74,



R = H (**1,4,7**), 2-OCH_3 (**2,5,8**), 4-OCH_3 (**3,6,9**)

Reagents and Conditions, (i) $SOCl_2$, reflux 2 hrs; (ii) NaOH, pyridine, room temperature; (iii) CH_3NHNH_2, ethanol, reflux



(**10**)

Scheme 1.

119.09, 118.91, 116.90, 116.85, 111.15, 103.24, 55.49, 37.19; MS m/z (%) 280.1(M^+, 100), 265.1 (13), 248.1 (31), 221.1 (20), 165.1 (9), 160.1 (17), 149.1 (15), 140.1 (14), 131.0 (12), 118.0 (11), 103 (8), 91 (13), 77 (6), 63 (3).

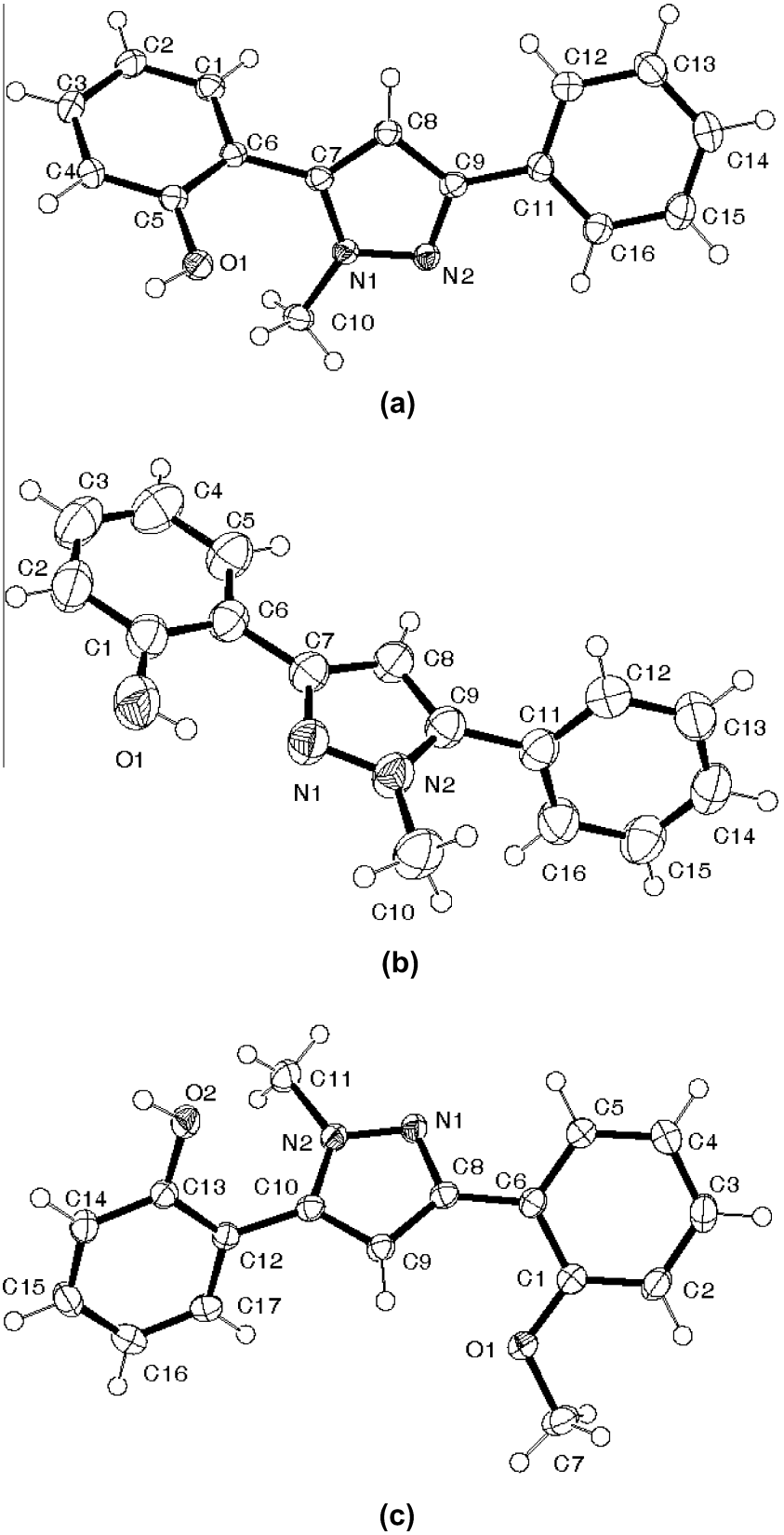


Fig. 2. ORTEP diagram of compounds (a) **7a**, (b) **7b** and (c) **8b.** Thermal ellipsoids have been drawn with 50% probability [27,28].

2.3. Single crystal X-ray diffraction studies

Single crystal X-ray diffraction data of compounds **7a, 7b, 8b** and **10** were collected at 173 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker Smart 1000 CCD diffractrometer. The data were collected using SMART and cell refinement and data reduction were carried out using SAINT [22]. The structure was solved with direct methods and refined by full matrix least square methods based on F^2 using SHELXS97 and SHELXL97 packages [23,24] (see Table 1).

3. Results and discussion

The synthesis of compounds **7–9a,b** is illustrated in Scheme 1. The preparation of the intermediate β-diketones **4–6** by the condensation of acid chlorides **1–3** and o-hydroxyacetophenone has already been reported [20,21]. The reaction of β-diketone with methyl hydrazine furnished corresponding regioisomeric pyrazoles **7–9a,b.** In the present study, three acids namely, benzoic acid, ortho-anisic acid and para-anisic acid were converted into their corresponding acid chlorides and the acid chlorides in each case were allowed to react with ortho-hydroxyacetophenone which resulted in β-diketones (**4–6**). Each β-diketone was then treated with methyl hydrazine in ethanol and refluxed till the completion of reaction. In case of β-diketones bearing no substituent **4** on phenyl ring and having a p-methoxy substituent i.e. **6**, the reaction occurred smoothly and the major product preferentially crystallized out from the reaction mixture. However, the other isomer was obtained by column chromatography. In case of β-diketone having an ortho-methoxy substituent **5** on the phenyl ring, the overall yield was very low under similar reaction conditions. However, when ortho-methoxyphenyl substituted β-diketone **5** was reacted under acidic conditions with methyl hydrazine, the yield was improved significantly with a marked decrease in reaction time. Moreover, an unexpected side product was also obtained, which was found to be **10** by X-ray crystallographic analysis. Probably the acetic acid used in the reaction had reacted with the methyl hydrazine and gave hydrazine which on reaction with β-diketone, resulted the compound **10**, however, the crystal structure of **10** is already reported, synthesized by different method [25].

3.1. Spectroscopic characterisation

The characteristic infrared bands of compounds **7–9**, υ(O—H), υ(C═N), υ(C═C) and υ(C—N), are at 3620–3605, 1640–1628, 1615–1600 and 1370–1360 cm^{-1}. In case of compounds **8** and **9** additional IR bands of υ(O—CH_3) group appeared at 1250–1230 cm^{-1}.

Table 2
Selected bond lengths (Å) and bond angles (°) for compounds **7a, 7b, 8b** and **10**.

Bond lengths (Å)		Bond angles (°)	
*Compounds **7a***			
C5—O1	1.357(2)	N1—C7—C8	106.26(15)
C7—N1	1.358(2)	N1—C7—C6	124.13(17)
C9—N2	1.340(2)	N2—C9—C8	110.45(16)
C10—N1	1.455(2)	N2—C9—C11	121.72(15)
N1—N2	1.360(2)	C7—N1—N2	112.18(15)
		C7—N1—C10	128.19(16)
*Compound **7b***			
C1—O1	1.3591(17)	O1—C1—C2	117.22(13)
C7—N1	1.3401(15)	O1—C1—C6	122.53(11)
C9—N2	1.3582(15)	N1—C7—C8	110.04(10)
C10—N2	1.4558(15)	N1—C7—C6	120.30(10)
N1—N2	1.3489(13)	N2—C9—C8	106.58(10)
		N2—C9—C11	122.59(10)
		C7—N1—N2	105.95(10)
		N1—N2—C9	111.73(10)
		N1—N2—C10	119.59(10)
		C9—N2—C10	128.58(11)
*Compound **8b***			
C1—O1	1.371(2)	O1—C1—C2	123.11(15)
C7—O1	1.431(2)	O1—C1—C6	116.59(14)
C8—N1	1.348(2)	N1—C8—C9	110.05(14)
C10—N2	1.358(2)	N1—C8—C6	119.25(14)
C11—N2	1.458(2)	N2—C10—C9	106.32(14)
C13—O2	1.3600(19)	N2—C10—C12	124.66(14)
N1—N2	1.3570(19)	O2—C13—C14	122.70(14)
		O2—C13—C12	117.44(14)
		C8—N1—N2	105.57(12)
		N1—N2—C10	112.04(13)
		N1—N2—C11	118.96(13)
		C10—N2—C11	128.98(14)
		C1—O1—C7	117.56(14)
*Compound **10***			
C5—O1	1.367(2)	N1—C7—C8	110.20(17)
C7—N1	1.343(2)	N1—C7—C6	118.73(16)
C9—N2	1.356(2)	N2—C9—C8	105.88(16)
C15—O2	1.371(2)	N2—C9—C10	123.85(16)
C16—O2	1.433(2)	O2—C15—C14	123.25(17)
N1—N2	1.347(2)	O2—C15—C10	116.17(16)
		C7—N1—N2	105.58(15)
		C15—O2—C16	118.02(16)

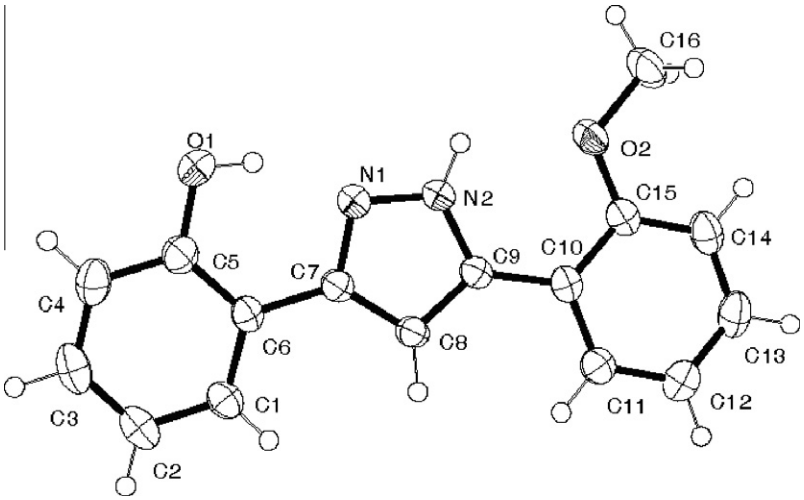


Fig. 3. ORTEP diagram of compound **10**. Thermal ellipsoids have been drawn with 50% probability [27,28].

In ^{1}H NMR spectra of regioisomers **7–9** only one resonance of pyrazole core are found as sharp singlet in the range 6.69–6.58 ppm depending on the nature of group attached to pyrazole core. The OH group signals are also appeared as singlets at 9.95–10.95 ppm. The other singlet resonances for N—CH_3 and O—CH_3 groups are in range of 3.58–3.88 ppm. The assignments of ^{13}C NMR signals of all regioisomers are straight forward and are assigned by comparison with related pyrazole analogues [18]. Methine carbon nuclei C-4 and two quaternary carbon nuclei C-3 and C-5 of pyrazole core fall in the range of 102–107 ppm and 141–151 ppm. The other carbon signals of substituted rings and N—CH3 group are appeared in the expected ranges comparable to analogous pyrazole derivatives [18].

All the regioisomers showed the molecular ion peak as base peak in the mass spectral analysis.

3.2. X-ray analysis of 7a, 7b, 8b and 10

The crystal structure of compounds **7a, 7b, 8b** and **10** are shown in Figs. 2 and 3. The crystal data and structure refinement details and selected bond lengths and bond angles are given in Tables 1 and 2 respectively.

In each case one isomer was obtained in large excess as compared to the other isomer. The formation of **7a, 8a** & **9a** as major isomer could be understood by the fact that the C=O group adjacent to the phenyl or substituted phenyl ring is relatively more electrophilic as compared to the C=O group next to the phenol ring. Therefore, nucleophile preferentially attack this C=O group. On the other hand, in case of substituted hydrazines, the substituent on Nitrogen of hydrazine reduces the accessibility of substituted Nitrogen by creating steric hindrance, therefore terminal

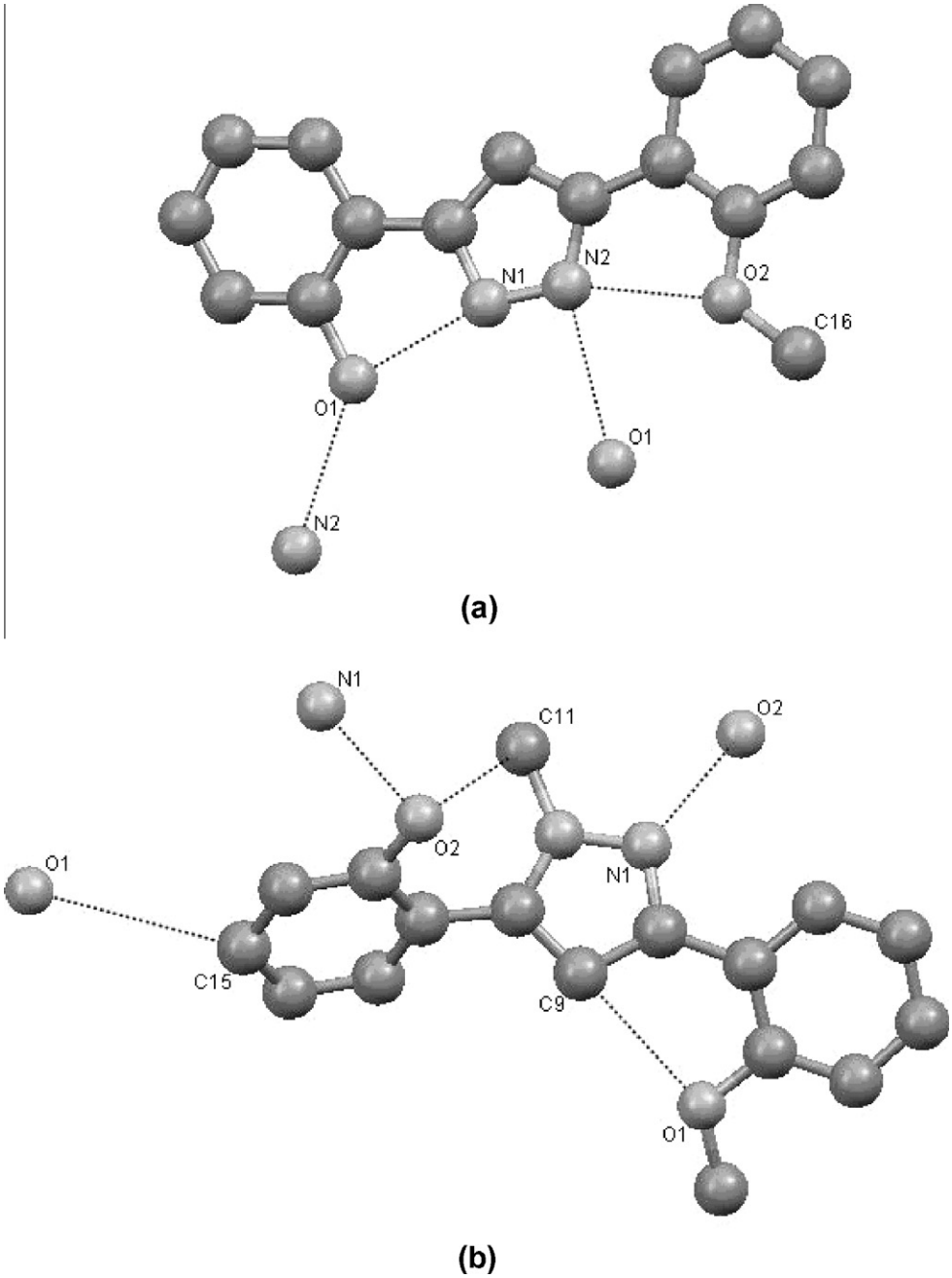


Fig. 4. Intra- and intermolecular hydrogen bonding in (a) **10** and (b) **8b** [29].

amino group of substituted hydrazine attacks the C=O carbon next to the substituted phenyl ring. This behaviour is further confirmed by the X-ray crystallographic studies of regioisomers **7a** and **7b**. The torsion angle between pyrazole ring and the hydroxyl substituted phenyl ring in **7a** is 56.51°, whereas the other phenyl ring is nearly coplanar with the pyrazole ring. In case of **7b** the situation is quite reverse and hydroxyl substituted phenyl ring is almost coplanar with the pyrazole ring. The other phenyl ring makes a torsion angle of 73.3° with the pyrazole ring. In case of **8b** both hydroxyl phenyl ring and methoxyphenyl ring are non-planar with the pyrazole ring as form torsion angle of 25.1° and 120.1° with central pyrazole ring respectively. The crystal structure of **10** [25] reveals that whole molecule is essentially planar. The molecule is organised in the crystal lattice by intra- and intermolecular hydrogen bonding. Intramolecular hydrogen bonds (O1—H1···N1 and N2—H2···O2) result in pseudo six membered rings as shown in Fig. 4a. Intermolecular hydrogen bonding, N2—H2···O1 forms layer constituted by hydrogen bonded dimer (Fig. 4a). This hydrogen bond is 2.882(2) Å longer than the intramolecular hydrogen bonding distances. In case of **8b** classic intermolecular hydrogen bonding O2—H2B···N1 is present in addition to the non-classic inter- and intramolecular hydrogen bonding involving C—H···O interactions (Fig. 4b).

The hydrogen bonding pattern is also observed in the compounds **7a** and **7b**. In **7a** intermolecular hydrogen interaction O1—H1B···N2 result in hydrogen bonded dimer (Fig. 5a). The non-classic hydrogen bonding, C10—H10C···O1, result in intramolecular interaction. In case of **7b** only one type of intramolecular hydrogen bonding (O1—H1B···N1) is observed which result in pseudo six membered ring (Fig. 5b). This is interesting to note that due to presence of methyl group on nitrogen atom adjacent to hydroxyl phenyl ring intermolecular hydrogen bonding is observed between OH group and nitrogen of pyrazole ring of other molecule in **7a** while in **7b** methyl group is present on nitrogen atom of

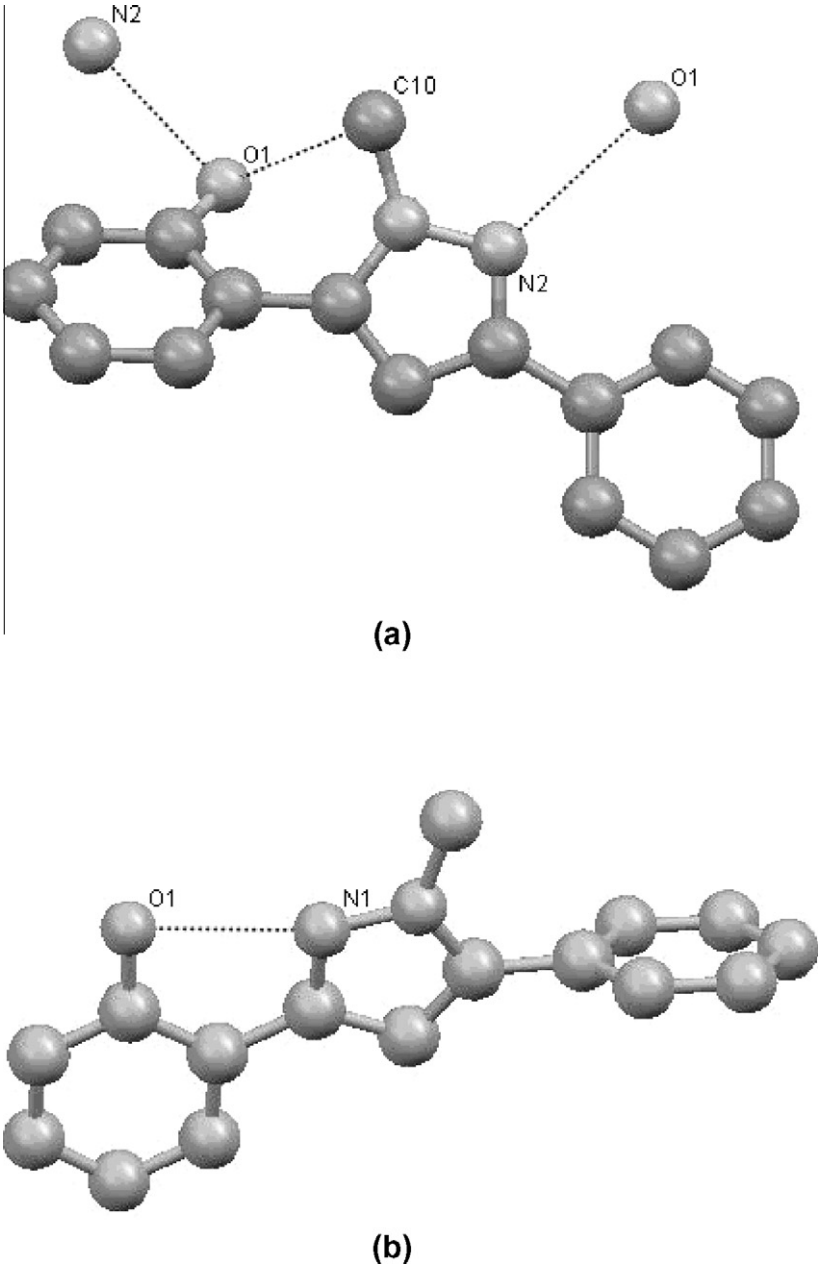


Fig. 5. Intra- and intermolecular hydrogen bonding in (a) **7a** and intramolecular hydrogen bonding in (b) **7b** [29].

pyrazole ring adjacent to phenyl ring which allow intramolecular hydrogen bonding. All bond lengths and angles in pyrazole and substituted phenyl rings are within the normal values [26].

4. Conclusions

Reaction of β-diketone **4–6** with methyl hydrazine results in regioisomeric 1,3,5-trisubstituted pyrazoles **7–9** which are characterised by spectroscopic techniques. Further crystal structure of compounds **7a, 7b** and **8b** are also determined. During the synthesis of compounds **8** addition of trace amounts of acetic acid results in the unexpected compound **10** which is characterised by the single crystal analysis.

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Appendix A. Supplementary data

Supplementary material Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 699636 for the compound 7a, CCDC No. 708765 for the compound 7b, CCDC No. 708766 for the compound 8b and CCDC No. 699637 for the compound 10. Copies of these information may be obtained on request from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.04.014.

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