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Synthesis, spectral, crystal and theoretical studies of some novel 4-heterocyclic substituted pyrazolones

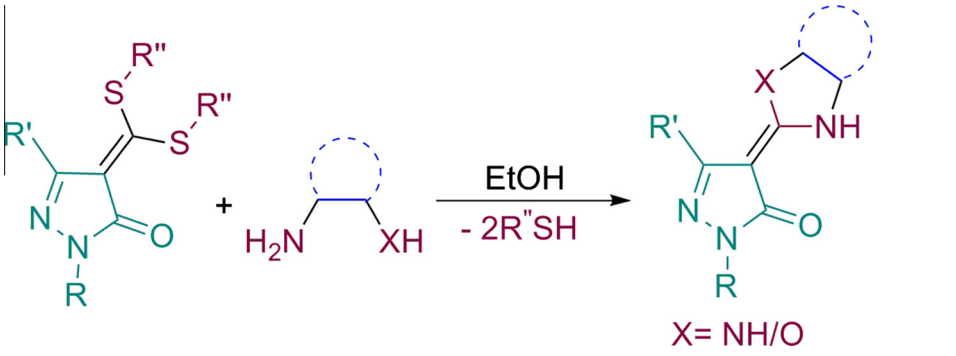
Kuppusamy Narayanan [a], Mani Shanmugam [a], Gnanasambandam Vasuki [b], Senthamaraikannan Kabilan [a,*]

[a] Department of Chemistry, Annamalai University, Annamalainagar 608002, Tamil Nadu, India
[b] Department of Chemistry, Pondicherry University, Kalapet, Puducherry 605014, Tamil Nadu, India

HIGHLIGHTS

- Pyrazolone ketene dithioacetals were synthesised by mild/PTC/strong bases.
- Regioselective products were obtained from dithioacetals reacting with 1,2-binuclephiles.
- Biologically potent imidazole/oxazole fused pyrazolones were synthesized.
- Compounds **3a-i** were characterized by IR, NMR and X-ray diffraction techniques.
- Theoretical data of **3e** by B3LYP/6-31G** method gives best fit with X-ray data.

GRAPHICAL ABSTRACT



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ABSTRACT

Reactions of pyrazolone ketene dithioacetals with various binucleophiles afforded 4-heterocyclic substituted pyrazolone compounds as ketene *N,N*-, *N,O*-acetals in the absence of any acid/base catalyst in good yields. The products **3a–i** formed by the direct displacement of dithioacetals exhibited high regioselectivity towards binucleophiles. All the synthesized compounds were characterized by IR, ^{1}H, ^{13}C, 2D NMR and X-ray diffraction techniques. Optimized geometry of compound **3e** has been computed by Density Functional Theory (DFT) method in B3LYP 6-31G** level basis set. The title compounds **3d–f** were crystallized in monoclinic space group Pc, $P2_1/n$, $P2_1/c$ with cell parameters: $a = 7.6647(3)$, $b = 26.7020(8)$, $c = 12.8364(5)$ Å, $\beta = 102.842(4)°$, $V = 2561.42(16)$ Å^3, $Z = 9$ (for **3d**), $a = 13.448(5)$, $b = 7.539(5)$, $c = 14.832(5)$ Å, $\beta = 94.747(5)°$, $V = 1498.6(12)$ Å^3, $Z = 4$ (for **3e**) and $a = 13.6468(17)$, $b = 15.905(2)$, $c = 7.9029(9)$ Å, $\beta = 100.774(9)°$, $V = 1685.1(4)$ Å^3, $Z = 4$ (for **3f**) respectively. The spectral and crystal studies revealed that the compounds **3a–i** exist in amine-one tautomeric form in solid state and the optimized structure **T5** of the compound **3e** exhibit good agreement with X-ray diffraction data.

1. Introduction

Pyrazolone is a five membered lactum ring compound containing two nitrogens which is an active ingredient of many drugs, especially in the class of nonsteroidal anti-inflammatory agents used in the treatment of arthritis and other musculoskeletal and joint disorders. The term of pyrazolone is sometimes used to refer anti-inflammatory agents [1,2]. The structures of a few drugs with pyrazolone as one of the component [3] are shown in (Fig. 1). NH-substituted 3-pyrazolin-5-ones are important targets as a consequence of their prevalence in numerous pharmaceuticals, agrochemicals, dyes and pigments as well as chelating and extracting agents [4,5]. Moreover pyrazolones with a heterocycle

* Corresponding author. Tel.: +91 9443924629.
E-mail address: kabilan60@sify.com (S. Kabilan).

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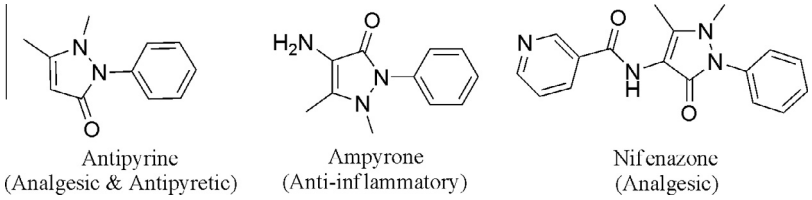


Fig. 1. Structures of a few drugs with pyrazolone moiety.

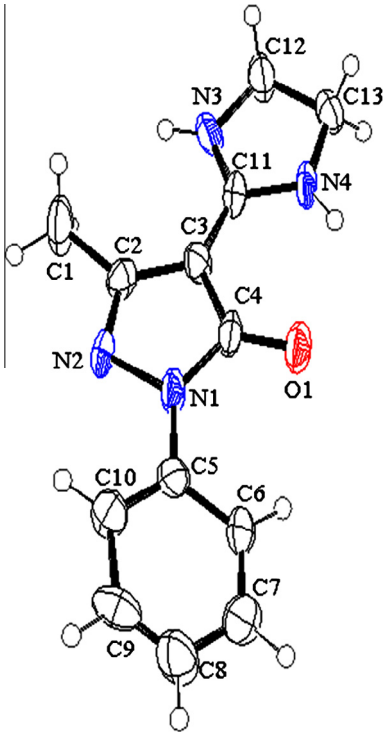


Fig. 2. Crystal structure of the compound **3d**.

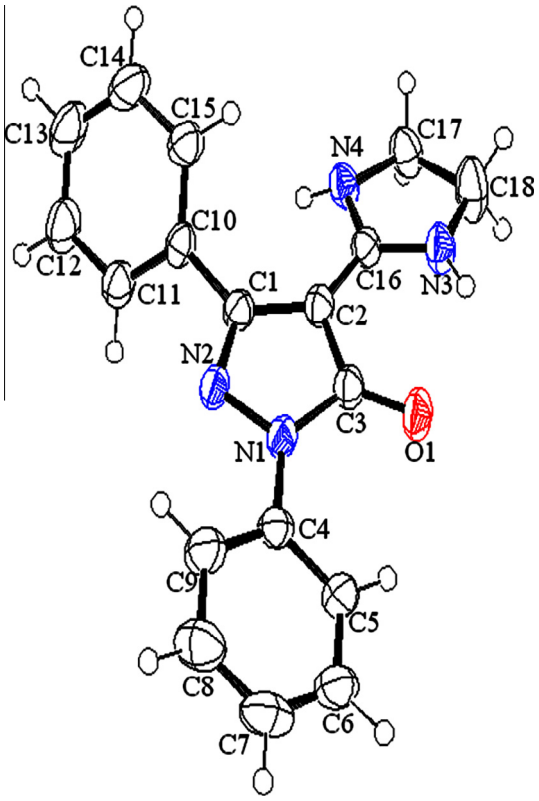


Fig. 3. Crystal structure of the compound **3e**.

substituent either at C-4 or C-3 are behave as kinase inhibitors [6,7]. Particularly, they are found to inhibit a class of enzymes that function in the catalysis of phosphoryl transfer reactions. Therefore, heterocycle substituted pyrazolones can be effective against targets in central nervous system disorders (Alzheimer disease), inflammatory disorders (psoriasis), bone diseases (osteoporosis), cardiac diseases (atherosclerosis, restenosis and thrombosis), metabolic disorders (diabetes) and infectious diseases such as viral and fungal infections. A few heterocycle substituted pyrazolones that are inhibitors of protein kinases such as vascular endothelial growth factor receptor (VEGFR) kinase, trkA tyrosine kinase (trkA), mixed lineage kinase (MLK) or fibroplast growth factor receptor kinase.

Pyrazolones are readily synthesized by condensation between β-ketoester and hydrazine hydrate. The physical and chemical properties of pyrazolones are modulated by their tautomeric property. In the case of 3-phenyl-5-pyrazolones, the nucleophilic character and the basicity of the nitrogen atoms change from tautomer to tautomer [8]. The hydrogen on C-4 can be readily deprotonated, generating a carbon nucleophile. Ketene dithioacetals have become an important synthon in organic chemistry and it can be readily prepared by reaction between a carbon nucleophile and carbon disulphide. The sulphur atom exercises the stabilizing effect on neighboring positive as well as negative species. This makes the double bond in ketene dithioacetals responsive towards both nucleophilic as well as electrophilic attack; an extremely useful feature for organic synthetic purposes. The synthesis of ketene dithioacetals and their applications in manipulation of the functionality or in the synthesis of heterocyclic system has been extensively investigated and reviewed [9–17].

In our present investigation various new heterocycle substituted pyrazolones have been synthesized with the reported [18–21] synthons and with 1,2-binucleophiles. Especially, dithioacetals in 3-methyl-1H-phenylpyrazolone derivative, we improved the synthesis of ketene dithioacetals in the absence of strong bases. Moreover the reported reactions were carried out only with 3-methyl-1H-phenylpyrazol-5-one. However the reaction of 4-(bis(methylthio)methylene)-3-methyl-1H-pyrazol-5-one/4-(bis(methylthio)methylene)-1,3-diphenyl-1H-pyrazol-5(4H)-one with aliphatic 1,2-binucleophile are not reported. Similar reactions with 3-methyl-1H and 3-phenyl-1H-phenylpyrazolone isomers are not also known. Hence in the present work it was proposed to synthesize heterocyclic substituted pyrazolones using ketene dithioacetals and to investigate their preferred tautomeric existence by the crystal structure.

2. Experimental

2.1. Synthesis of pyrazolone ketene dithioacetals

2.1.1. Preparation of 4-(1,3-dithiepan-2-ylidene)-3-methylpyrazol-5-one (**2a**)

In a 100 mL round bottom flask fitted with air condenser, a suspension of 3-methyl-1H-pyrazol-5-one (**1b**) (0.01 mol), anhydrous potassium carbonate (0.02 mol), tetrabutylammonium bromide (TBAB) (0.003 mol) and carbon disulfide (10 mL) in dry acetonitrile (50 mL) was efficiently stirred at room temperature for 30 min. To the reaction mixture dibromobutane (0.03 mol) was added, stirred constantly at 25 °C. The reaction progress was monitored by TLC over the entire reaction period. After completion of the reaction, the residue obtained was filtered and washed with 50 mL of ice-cold water. The pH of the solution was checked and neutralized with 10% diluted hydrochloric acid. The yellow solid thus obtained was purified by recrystallization with ethanol. Yield: 55%; m.p: 198 °C; lit m.p: 195–196 °C [20].

2.1.2. Preparation of 4-(bis(methylthio)methylene)-3-methyl-1-phenyl -1H-pyrazol-5(4H)-one (**2b** & **2C**)

3-Methyl-1H-phenylpyrazol-5-one (**1b**) (0.036 mol) and triethylamine (0.072 mol) were dissolved in 15 mL of dimethyl sulfoxide in a 250 mL round bottom flask. Carbon disulfide (0.036 mol) was added drop wise slowly through a pressure-equalizing funnel to the mixture at room temperature with vigorous stirring. After 10 min, methyl iodide (0.072 mol) was added and the reaction mixture was maintained at 0 °C and stirred for 30 min. Yellow solid (hemithioacetals) was formed and filtered. The remaining filtrate was separated by chloroform–water mixture and the organic layer was dried using anhydrous sodium sulphate. Solvent was removed and the crude was purified by column chromatography (Silica gel, hexane/ethyl acetate 8:2). Two products were isolated from the mixture that was found to be yellow solid as hemithioacetal (m.p: 92–95 °C, Yield: 55%) and red colored syrupy semisolid as dithioacetal (m.p: 62–65 °C, Yield: 29%). For compound **2c** preparation, **1c** with sodium hydride (NaH) base in dry tetrahydrofuran (THF) sovent medium was used and the above same procedure was followed. (Note: pyrazolone hemithioacetal further converted into dithioacetal by methylation in DMF/triethylamine/MeI reagent; Yield: 84%) [21].

2.2. Synthesis of benzimidazole substituted pyrazolone

2.2.1. Synthesis of 4-(1H-benzo[d]imidazol-2-yl)-5-methyl-1H-pyrazol -3(2H)-one (**3a**)

4-(1,3-Dithiepan-2-ylidene)-3-methyl-1H-pyrazol-5(4H)-one (**2a**) (0.114 g, 0.5 mmol) and 1,2-phenylenediamine (0.054 g, 0.5 mmol) in ethanol (7 mL) were refluxed for 5 h. The colorless solid thus obtained was filtered and washed with cold ethanol. Further it was recrystalized from methanol. Yield: 33%, m.p:174–175 °C. IR (cm^{-1}): 3402, 3262 (NH), 2978 (C–H), 1576, 1510 (C=C/C=N), 1634 (C=O) ^{1}H NMR δ (ppm) (400 MHz): ($CDCl_3$): 2.48 (3H, s), 4.76 (3H, s), 7.12 (2H, dd), 7.53 (2H, dd). ^{13}C NMR δ (ppm) (100 MHz): 12.88, 140.96, 90.5, 162.33, 90.94, 147.49, 135.96, 113.56, and 121.56.

2.3. Synthesis of benzoxazole substituted pyrazolone

2.3.1. Synthesis of 4-(benzo[d]oxazol-2-yl)-5-methyl-1H-pyrazol-3(2H) -one (**3b**)

A mixture of 4-(1,3-dithiepan-2-ylidene)-3-methyl-1H-pyrazol-5(4H)-one (**2a**) (0.114 g, 0.5 mmol), 2-aminophenol (0.054 g, 0.5 mmol) was refluxed in ethanol (7 mL) for 3 h. The colorless precipitate was filtered and washed with cold ethanol. The compound was purified by recrystallization with methanol. Yield: 38%. m.p: 248 °C. IR (cm^{-1}): 3461 (NH), 3166, 3062 (C–H), 1578, 1515 (C=C/C=N), 1657 (C=O). ^{1}H NMR δ (ppm) (400 MHz): (DMSO-d_6 + $CDCl_3$): 2.65 (3H, s), 4.25 (NH), 7.64 (1H, d), 7.55 (1H, d), 7.32 (2H, t). ^{13}C NMR δ (ppm) (100 MHz): 159.93, 91.24, 160.86, 11.5, 148.65, 140.45, 140.05, 123.74, 123.08, 117.74, and 109.51.

2.4. synthesis of imidazole substituted pyrazolone

2.4.1. Synthesis of 4-(4,5-dihydro-1H-imidazol-2-yl)-5-methyl-1H-pyrazol-3(2H)-one (**3c**)

A mixture of 4-(1,3-dithiepan-2-ylidene)-3-methyl-1H-pyrazol-5(4H)-one (**2a**) (0.114 g, 0.5 mmol) and ethylenediamine (0.031 g, 0.5 mmol) was refluxed in ethanol (7 mL) for an hour. After cooling, solvent was evaporated in a rotary evaporator. The crude precipitate obtained was purified by crystallization in ethanol. Yield: 49%, m.p: >300 °C. IR (cm^{-1}): 3304 (NH), 3123, 2946 (C–H), 1594 (C=C/C=N), 1641 (C=O). ^{1}H NMR δ (ppm) (400 MHz): (D_2O): 2.23 (3H, s), 2.25 (NH), 3.78 (4H, s). ^{13}C NMR δ (ppm) (100 MHz): 137.66, 85.18, 160.71, 14.04, 148.62 and 42.87.

2.4.2. Synthesis of 4-(imidazolidin-2-ylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (**3d**)

A mixture of 4-(bis(methylthio)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (**2b**) (0.278 g, 1 mmol) and ethylenediamine (0.06 g, 1 mmol) was vigorously stirred in ethanol at room temperature for 10 min. The colorless precipitate was filtered and crystallized from methanol. Yield: 41%. m.p: 138–140 °C. IR (cm^{-1}): 3410 (NH), 2971 (C–H), 1500 (C=C/C=N), 1656 (C=O). ^{1}H NMR δ (ppm) (400 MHz): (DMSO-d_6 + $CDCl_3$): 2.32 (3H, s), N-Ph 8.01 (2H, d), 7.31 (2H, t), 7.04 (1H, t) 8.20 (1H, s), 3.76 (4H, s). ^{13}C NMR δ (ppm) (100 MHz): 159.62, 84.39, 164.84, 14.54, N-Ph 139.10, 127.37, 122.19, 117.6, 144.79 and 42.13.

2.4.3. Synthesis of 4-(imidazolidin-2-ylidene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**3e**)

4-(Bis(methylthio)methylene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**2c**) (0.340 g, 1 mmol) and ethylenediamine (0.06 g, 1 mmol) were vigorously stirred in ethanol at 60 °C for 5 min. The colorless precipitate obtained was filtered and crystallized from ethanol. Yield: 51%. m.p: 260–262 °C; IR (cm^{-1}): 3277 (NH), 2933 (C–H), 1599, 1478 (C=C/C=N), 1641 (C=O). ^{1}H NMR δ (ppm) (400 MHz): (DMSO-d_6): 3.61 (4H, s, N$\underline{CH_2CH_2}$N), 8.03 (2H, s, NH); Aryl protons: 7.10 (1H, t), 7.37 (2H, t), 7.46 (2H, t) 7.57 (2H, d), 8.08 (2H, d); ^{13}C NMR δ (ppm) (100 MHz): 43.07, 165.27, 148.36, 83.14, 159.87; Aryl carbons: 118.03, 123.29, 127.92, 128.41, 128.51, 128.67, 133.91, 140.04.

2.4.4. Synthesis of 4-(1H-benzo[d]imidazol-2(3H,3aH,4H,5H,6H,7H,7aH)-ylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (**3f**)

4-(Bis(methylthio)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (**2b**) (0.278 g, 1 mmol) was treated with (1R, 2R)-diaminocyclohexane (0.114 g, 1 mmol) in ethanol (20 mL) for 5 h. The solid obtained was filtered and recrystallized from ethyl acetate. Yield: 54%. m.p: 130–132 °C; IR (cm^{-1}): 3410 (NH), 2971 (C–H), 1500 (C=C/C=N), 1656 (C=O). ^{1}H NMR δ (ppm) (400 MHz): ($CDCl_3$): 2.34 (3H, s), N-Ph 8.00 (2H, d), 7.35 (2H, t), 7.11 (1H, t), 9.09 & 5.66 (NH), 3.19 (2H, q, CH), 1.36 (2H, m), 1.54 (2H, m), 1.87 (2H, m), 1.87 (2H, m), 2.16 (2H, m). ^{13}C NMR δ (ppm) (100 MHz): 145.06, 86.70, 162.04, 15.83, N-Ph 139.72, 128.57, 123.81, 119.07, 166.10, 62.35, 28.95, 23.86 and 15.83.

*2.4.5. Synthesis of 4-(1H-benzo[d]imidazol-2(3H,3aH,4H,5H,6H, 7H,7aH)-ylidene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**3g**)*

4-(Bis(methylthio)methylene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**2c**) (0.340 g, 1 mmol) was treated with (1R,2R)-diaminocyclohexane (0.114 g, 1 mmol) in ethanol (20 mL) for 15 min. The solid obtained was filtered and recrystallized from ethanol. Yield: 58%. m.p: 262–264 °C; IR (cm^{-1}): 3425, 3230 (NH), 2931 (C–H), 1596, 1566, 1498 (C=C/C=N), 1642 (C=O). ^{1}H NMR δ (ppm) (500 MHz): (DMSO d_6): 8.280(NH), All aryl protons: 7.10 (1H,t), 7.38 (2H, t), 7.48 (3H, m), 7.59 (2H, d), 8.09 (2H, d); Alkyl protons: 3.10 (2H, q), 2.15 (2H, d), 1.73 (2H, d), 1.40 (2H, m), 1.28 (2H, m); ^{13}C NMR δ (ppm) (125.7 MHz): 24.05, 29.16, 62.94, 148.91, 84.71, 162.30, 165.83; Aryl Carbons: 118.53, 123.84, 128.42, 129.01, 129.16, 134.41 and 140.47.

2.5. Synthesis of oxazole substituted pyrazolone

*2.5.1. Synthesis of 3-methyl-4-(oxazolidin-2-ylidene)-1-phenyl-1H-pyrazol-5(4H)-one (**3h**)*

A mixture of 4-(bis(methylthio)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (**2b**) (0.278 g, 1 mmol) and ethanolamine (0.061 g, 1 mmol) was vigorously stirred in ethanol at RT for 30 min. The colorless solid obtained was purified by recrystallization from ethyl acetate. Yield: 48%. m.p: 182–185 °C; IR (cm^{-1}): 3300, 3261 (NH), 2972 (C–H), 1535, 1490 (C=C/C=N), 1673 (C=O). ^{1}H NMR δ (ppm) (400 MHz): ($CDCl_3$): 2.30 (3H, s), Aryl protons: 8.01 (2H, d), 7.36 (2H, t), 7.11 (1H, t), 6.90 (NH), 3.76 (2H, t), 4.59 (2H, t). ^{13}C NMR δ (ppm) (100 MHz): 146.99, 85.86, 166.39, 15.24, Aryl carbons: 139.63, 128.59, 123.93, 119.10, 166.0, 69.30 and 42.66.

*2.5.2. Synthesis of 4-(oxazolidin-2-ylidene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**3i**)*

A mixture of 4-(bis(methylthio)methylene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**2c**) (0.340 g, 1 mmol), ethanolamine (0.061 g, 1 mmol) was refluxed in ethanol at 60 °C for 10 min. Solvent was removed under vacuum and the solid separated was washed with cold ethanol. The colorless solid obtained was purified by recrystallization from ethanol. Yield 68%.m.p: 218–220 °C. IR (cm^{-1}): 3420 (NH), 2923 (C–H), 1593, 1540 (C=C/C=N), 1653 (C=O). ^{1}H NMR δ (ppm) (400 MHz): ($CDCl_3$ + $DMSOd_6$): 4.65 (4H, s, OCH_2CH_2N), Aryl protons: 7.10 (2H, t), 7.63 (4H, s), 8.01 (4H, d), 8.06 (NH); ^{13}C NMR δ (ppm) (100 MHz): 42.74, 69.86, 148.23, 83.26, 165.31, 165.74; Aryl Carbons: 118.45, 123.88, 127.73, 128.24, 128.35, 128.48, 133.10, 139.31 and 148.23.

The synthesis of the all the compounds (**3a–i**) can be summarized in Scheme 1 and their product formations from their respective ketene dithioacetals are listed in Table 1.

2.6. Spectral measurement

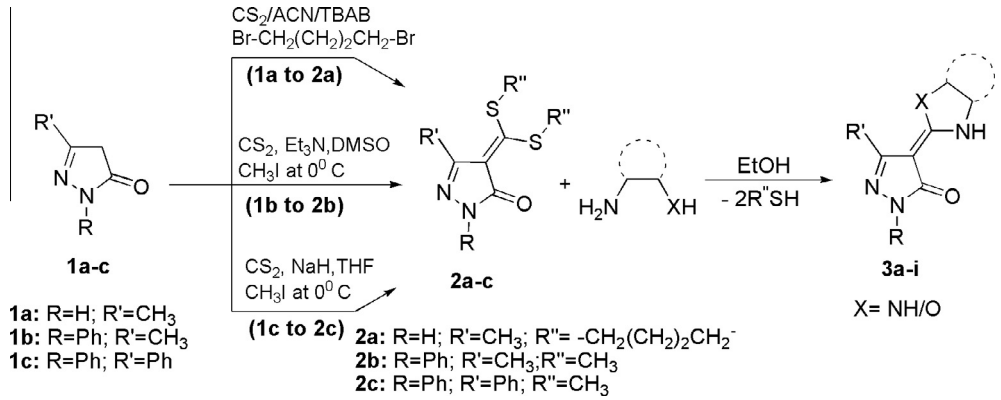
All the reagents and solvents were purchased from Aldrich, E-Merck or Sisco Chemicals, India. Melting points were recorded on Gallemkamp melting point apparatus and were uncorrected. IR spectra were recorded in a spectral range 4000–400 cm^{-1} using KBr pellets in Nicolet 6700 FT-IR and ABB Bomem MB 104 FT-IR spectrometer. ^{1}H NMR spectra were recorded on 400 MHz, Bruker AVENCE 400 MHz spectrometer using $CDCl_3$, DMSO-d_6 and its mixture as solvent with TMS as the internal standard. ^{13}C NMR spectra were recorded on 100 MHz, Bruker AVENCE 400 MHz spectrometer using $CDCl_3$, DMSO-d_6 and its mixture as solvent with TMS as the internal standard.

2.7. X-ray determination

Single crystals were obtained by the slow evaporation of compound **3d–f** in ethanol. The colorless crystals of the compound with appropriate dimensions were mounted on a glass fiber with epoxy cement for the X-ray crystallographic study. Table 2 lists the crystallographic data and data collection parameters of the compounds **3e–f** which were collected at 293 K in Oxford Diffraction Xcalibur CCD Eos diffractometer (for **3d**) and Bruker axs kappa apex2 CCD diffractometer (for **3e** & **3f**) equipped with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source was used for the measurement of data. Data collection, cell refinements and data reduction were performed using the CRYSALISPRO [22] (for **3d**) and SAINT [23] (for **3e** & **3f**) softwares. Molecular graphics employed include ORTEP [24] and PLATON [25] programs. The structures of all the compounds (**3d–f**) were solved by the direct method and Full-matrix least-squares refinement on F2 with anisotropic thermal parameters was carried out by (SHELXL-97) [26]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and the positional parameters were refined using riding model.

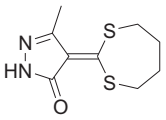
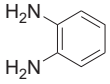
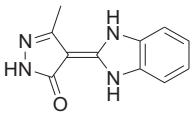
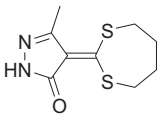
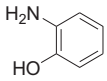
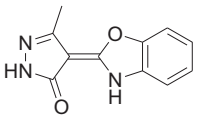
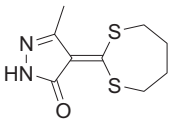
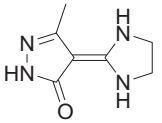
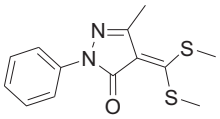
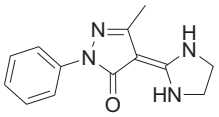
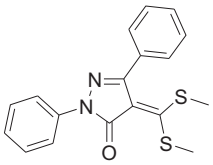
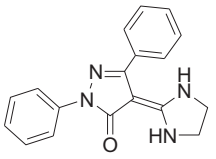
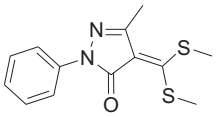
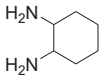
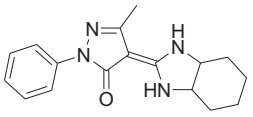
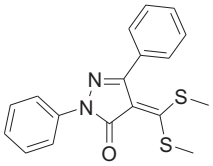
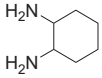
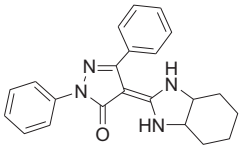
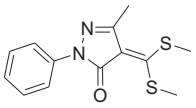
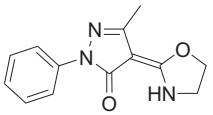
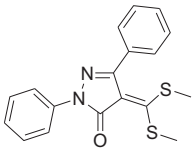
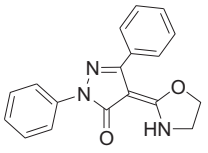
2.8. Computational details

Theoretical calculations were performed at DFT levels on a Xeon processor E3-1225, V2 quardcore, 3.20 GHz personal computer using Jaguar software package, version 8.0, Schrodinger, LLC, New York. The geometry of 4-(imidazolidin-2-ylidene)-1,3-diphenyl-1H-pyrazol-5(4H)-one (**3e**) was optimized by Density Functional Theory (DFT) method (B3LYP) with standard 6-31G** basis set. The resulting geometry, bond length and bond angles were compared with the existing experimental data. Also HOMO,



Scheme 1.

Table 1
Illustration of the product formation (**3a–i**) from the respective reactants.

Reactant	Binucleophile	Compound	R	R'	Structure
		**3a**	H	CH_3	
		**3b**	H	CH_3	
		**3c**	H	CH_3	
		**3d**	Ph	CH_3	
		**3e**	Ph	Ph	
		**3f**	Ph	CH_3	
		**3g**	Ph	Ph	
		**3h**	Ph	CH_3	
		**3i**	Ph	Ph	

LUMO energies were calculated for various tautomeric form of compound **3e**.

3. Results and discussion

All the synthesized compounds were characterized by IR, ^{1}H NMR and ^{13}C NMR spectra.

3.1. IR spectral studies

IR spectral data indicate the presence of characteristic functional groups present in the title compounds. For all the compounds (**3a–i**), stretching frequency around 3261–3461 cm^{-1} and 1631–1673 cm^{-1} are assigned for NH of the newly formed heterocycle at C4 carbon and pyrazolone amide C=O functional groups, respectively. The above NH and C=O stretching frequency (the absence of OH stretching frequency around 3450–3650 cm^{-1}) reveals that pyrazolone amide carbonyl which is preferable in amine-one form [27,28] rather than imine-ol form and involves in the intramolecular hydrogen bonding with NH of the newly formed heterocycles [29]. Aromatic C–H stretching bands appear in the region 2971–3123 cm^{-1}. In addition, the C=N and C=C stretching frequencies appear at 1576–1598 cm^{-1} and 1495–1515 cm^{-1} respectively.

3.2. ^{1}H NMR spectral studies of compounds *3a–i*

The compound **3a–c** were obtained from 4-(1,3-dithiepan-2-ylidene)-3-methylpyrazol-5-one react with 1,2-diaminobenzene, 2-aminophenol and 1,2-diaminoethane, respectively in good yield. The above three compounds only differ by their N,N-acetal and N,O-acetal from the parent NH pyrazolone ring. ^{1}H NMR spectra

Table 2
Summary of crystallographic data of **3d–f**.

Compound	**3d**	**3e**	**3f**
Emprical formula	C_{13} H_{14} N_4 O	C_{18} H_{16} N_4 O	C_{17} H_{20} N_4 O
Formula weight (g mol^{-1})	242.28	304.34	296.37
Crystal system (space group)	P c, monoclinic	$P2_1/n$, monoclinic	P $2_1/c$, monoclinic
Wave length (Å)	0.71073	0.71073	0.71073
a (Å)	7.6647(3)	13.448(5)	13.6468(17)
b (Å)	26.7020(8)	7.539(5)	15.905(2)
c (Å)	12.8364(5)	14.832(5)	7.9029(9)
α (°)	90.00	90.000(5)	90.00
β (°)	102.842(4)	94.747(5)	100.774(9)
γ (°)	90.00	90.000(5)	90.00
Volume (A^3)	2561.42(16)	1498.6(12)	1685.1(4)
Z, D_{calc} (Mg/m^{-3})	9, 1.414	4, 1.344	4, 1.168
Absorption coefficient (mm^{-1})	0.095	0.087	0.076
F(000)	1152	636	632
Theta range for data collection (°)	2.73–25.00	1.00–24.99	1.99–25.00
Reflection collected/unique	22961/8825 [$R_{(int)}$ = 0.0608]	13721/2630 [$R_{(int)}$ = 0.0425]	16711/2964 [$R_{(int)}$ = 0.0591]
Goodness of fit	0.738	1.093	0.886
Data/restraints/parameter	8825/14/709	2630/0/272	2964/0/232
Completeness to theta = 25.00°	99.9%	99.9%	99.9%
Refinement method	Full-matrix least squares on *F*^2	Full-matrix least squares on *F*^2	Full-matrix least squares on *F*^2
R indices (all data)	R_1 = 0.1077, wR_2 = 0.2137	R_1 = 0.0498, wR_2 = 0.1106	R_1 = 0.1996, wR_2 = 0.1671
Final *R* indices [$I > 2$ sigma(I)]	R_1 = 0.0608, wR_2 = 0.1615	R_1 = 0.0425, wR_2 = 0.1044	R_1 = 0.0591, wR_2 = 0.1248
Limiting indices	$-8 \leqslant h \leqslant 9$, $-31 \leqslant k \leqslant 31$, $-15 \leqslant l \leqslant 15$	$-15 \leqslant h \leqslant 15$, $-8 \leqslant k \leqslant 6$, $-17 \leqslant l \leqslant 17$	$-13 \leqslant h \leqslant 16$, $-18 \leqslant k \leqslant 18$ $-9 \leqslant l \leqslant 9$
Largest diff. peak and hole (e $Å^{-3}$)	0.309 and −0.473	0.219 and −0.350	0.166 and −0.244

of the compound **3a–c** show a signal in the shielded region with three protons integral at 2.48 ppm, 2.65 ppm and 2.23 ppm as a sharp singlet, are respectively assigned for pyrazolone C3-methyl group. For compounds **3a** and **3b**, NH protons are appeared at 4.71 ppm and 4.25 ppm with three protons integral. However NH signals are not observed for **3c,** since the NH protons are exchangeable with D_2O solvent. Moreover in compound **3a** two signals in the aromatic region at 7.12 ppm (J = 6.0 Hz; 3.2 Hz) and 7.53 ppm (J = 5.6 Hz; 2.4 Hz) as doublet of doublet with two protons integral each suggest that they are chemical shift equivalent and magnetically non-equivalent protons. Whereas **3b**, a benzoxazole derivative, shows three peaks at 7.65 ppm (1H), 7.55 ppm (1H) and 7.32 ppm (2H) in the aromatic region which are due to the two different hetero atoms persist in the C4 benzoxazole aryl ring. In **3c**, imidazolyl heterocycle shows an intense signal at 3.78 ppm with four protons integral confirms the formation of –N–CH_2–CH_2–N– at C4 of the pyrazolone ring. Whereas introduction of an aryl group at N1 in **3d** and two aryl groups at N1 and C3 in **3e** show a singlet for –N–$\underline{CH_2}$–$\underline{CH_2}$–N– protons at 3.76 ppm and 3.61 ppm respectively, do not have much variation (3.78 ppm) with **3c**. Hence a singlet with four protons integral suggests that compound **3c–e** have two equivalent CH_2 groups adjacent to two NH protons (–$\underline{HN}CH_2CH_2\underline{NH}$–) on C4 heterocycle (Figs. 2 and 3). For compound **3f** & **3g** formation, 1R,2R-cyclohexyldiamine was used for the cyclization, thus resulted structures exhibit the diequatorial substitution on C4 pyrazolone (Fig. 4). Cyclohexyl group shows 5 sets of protons each with two integrals show that cyclohexyl ring adopts chair conformation with diequatorial amino substitution. Further compound **3h** and **3i** obtained from the cyclization with 2-aminoethanol, show two alkyl peaks in different chemical environments. For compound **3h** two triplets with two proton integrals at 4.59 ppm and 3.76 ppm are assigned to methylene protons of C4 heterocycle which are adjacent to the O and N hetero atoms respectively. Obviously, other aromatic protons of **3a–i** are observed in the region of 6.95–8.01 ppm with the respective integrals.

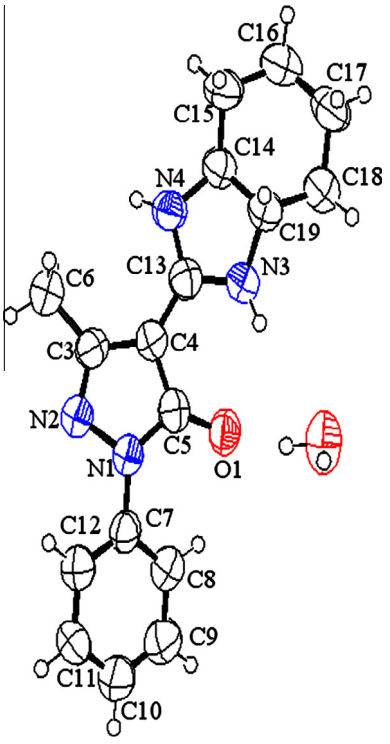


Fig. 4. Crystal structure of the compound **3f**.

3.3. ^{13}C NMR spectral studies of compounds *3a-i*

In all 3-methyl pyrazolone compounds (**3a–f**), C3-methyl carbon is observed in the region of 11.35–15.83 ppm and also pyrazolone amide carbonyl carbon is observed at 159.87–166.39 ppm in the down field region. Mainly intense signals observed in the regions at 42.87, 42.13 and 43.07 ppm are attributed to methylene carbons (NH–$\underline{CH_2}$–$\underline{CH_2}$–NH) of C4 imidazole compounds **3c, 3d**

and **3e**, respectively. Whereas C4 oxazole methylene carbons (O–CH_2–CH_2–NH) of compounds **3h** & **3i** exhibit, two signals at 42.66 & 42.74 ppm (O–CH_2–$\underline{CH_2}$–NH) and 69.30 & 69.86 ppm (O–$\underline{CH_2}$–CH_2–NH) respectively, are due to the two different hetero atoms adjacent to the methylene groups. Besides C4-cyclohexyl imidazole derivatives, (**3f** & **3g**) show three alkyl carbon peaks, in the region of 23.86, 28.95 & 62.01 ppm and 24.05, 29.16 & 62.94 ppm, respectively illustrate the presence of cyclohexyl moiety. Moreover, C4 benzimidazole (**3a**), benzoxazole (**3b**) are the aromatic heterocycle, thus their respective carbon signals are observed in the aromatic region at 118.03–129.16 ppm. Exclusively, chemical shift value of ring junction carbon C2' is varied by the presence of alkyl and aryl moiety on the C4 heterocycle. Hence C2' of benzimidazole and benzoxazole heterocycle (147.4–148.6 ppm) are slightly shielded (≈10–15 ppm) than the aliphatic C4 heterocycles (159.6–166.1 ppm).

3.4. 2D NMR spectral studies of compounds *3a* & *3h*

2D NMR spectra (HOMOCOSY, HSQC and HMBC) show the structural skeleton of the compound and support the formation of the compound **3a** and **3h**. HOMOCOSY spectra of compound **3a** shows HOMO correlation with two proton peaks at 7.12 ppm and 7.52 ppm, reveals that the above protons adjacent to one another, and hence these peaks are attributed to the H4',7' and H5',6', respectively. The chemical shift at 12.88 ppm is assigned for methyl carbon of the pyrazolone moiety, which also exhibit HSQC spectral correlation with methyl protons at 2.48 ppm. The hydrogen attached imidazolyl carbons are assigned at 113.56 ppm for C4',7' and 121.56 ppm for C5',6' ring carbons, since these peaks exhibit HSQC correlation with 7.12 ppm and 7.52 ppm, respectively. In HMBC spectrum, a chemical shift at 140.96 ppm and 90.94 ppm show α and β correlation with 3-Me protons at 2.48 ppm, hence these peaks are assigned to C3 and C4 of the pyrazolone ring, respectively. Also a peak at 135.96 ppm shows multiple bond correlation with 7.12 ppm and 7.52 ppm, is attributed to benzimidazole aryl ipso carbons (C8',9'). The chemical shift values 162.33 and 147.49 ppm do not correlate with any hydrogen in HMBC. So the most deshielded chemical shift value, 162.33 ppm is assigned to pyrazolone carboxyl carbon and 147.49 ppm assigned to C2' of benzimidazole ring junction carbon at C4 of the pyrazolone ring. Similarly, for an oxazole compound **3h**, a triplet at 3.76 ppm shows HOMO cross peak with another triplet at 4.59 ppm, which implies that both set of protons are adjecent to one another, hence these peaks are assignable to C4 oxazolidine methylene protons. DEPT spectrum also confirms the C4 heterocyclic formation by the inverted carbon peaks at 42.67 and 69.29 ppm. A peak at 8.02 ppm shows intense HOMO correlation with a triplet at 7.36 ppm and the later peak shows cross peak with 7.11 ppm, suggest that the peaks at 8.02, 7.36 & 7.11 ppm are assigned to *ortho*, *meta* and *para* protons, respectively. From the HMBC spectrum, a peak in the deshielded region, at 166.00 ppm shows intense β correlation with methylene protons at 3.76 and 4.59 ppm suggest that peak at 166.00 ppm is unambiguously assigned to C2' of the oxazole ring. In addition two carbon peaks 146.99 ppm and 85.86 ppm shows HMBC correlation with methyl protons at 2.303 ppm, suggest that the above peaks are respectively assigned to C2(C=N) and C3(C=C) of the pyrazolone ring. Moreover, N1 ipso carbon is assigned by the intense HMBC (α, β, γ) correlation with respective *ortho, meta and para* protons (Fig. 5). The structures of all the imidazoles as well as oxazoles are proposed by the similar spectral pattern exerted by these (**3a** & **3h**) molecules (Fig. 6).

Obviously, pyrazolone heterocycle exhibits various tautomeric forms in solution and hence its bond lengths are varied drastically. The stabilization of the imidazole/oxazole moiety and the greater

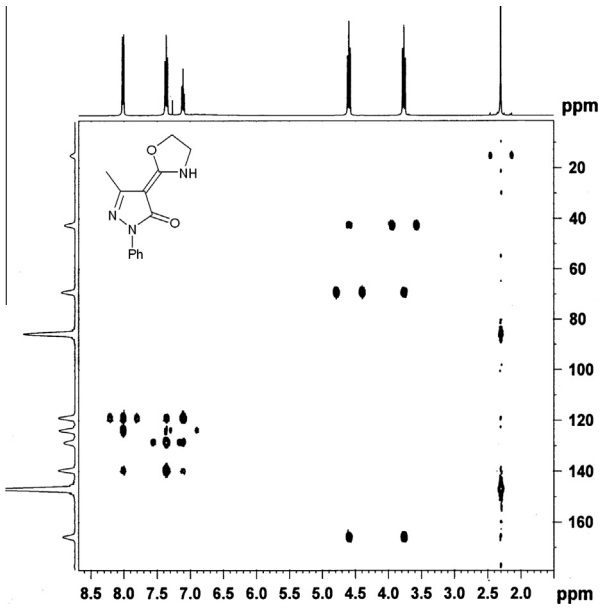


Fig. 5. HMBC spectrum of compound **3h**.

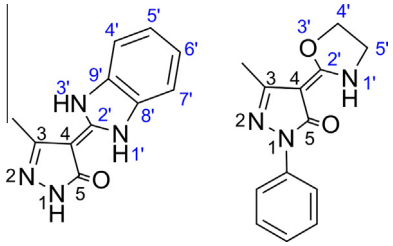


Fig. 6. Numbering of compounds **3a** & **3h**.

entropy by the free rotation between two heterocyclic systems might have unfavored for a single tautomer. The stability decides the reactivity improvement, in order that stable form of product must be identified. For instance, compound **3e** is taken into the consideration and this tautomerise into various forms (**T1**–**T5**) is shown in Fig. 7. The stable tautomer with lowest energy has been identified (**T5**) by DFT/B3LYP calculation and the physical parameters are compared with the structure obtained by the X-ray data.

4. Molecular structure determination from crystal data

The structural parameter of the compounds **3d–f** were determined by using single crystal X-ray diffraction technique. ORTEP diagram of compounds **3d–f** with the atomic numbering is shown in (Figs. 2–4). Theoretical study is computed and compared with crystal structure of compound **3e**. Compound **3e** is crystallized in a monoclinic system, with space group $P2_1/n$, $Z = 4$ and also with lattice parameters $a = 13.448(5)$, $b = 7.539(5)$, $c = 14.832(5)$ Å, $\beta = 94.747(5)^\circ$, volume 1498.6(12) Å^3. The selected bond length, bond angles of **3e** are also listed in (Table 3). The single crystal structure analysis provides evidence that the molecular structure of **3e** is very close to the similar reports by Li-Nan Li [30].

The C(3)–O(1) distance is 1.245(2) Å which is shorter than that for C–OH in some pyrazolone compounds 1.319(5) Å by Uzoukwu [31] and 1.313(2) Å by Holzer [32], whereas it is closer to the distance of C=O in similar compounds: 1.248(3) Å by Jing Li [33] and 1.245(4) Å by Vyas [34]. The C(2)–C(16) (1.408(2) Å) is shorter than the normal C–C bond length (1.53 Å), but close to C=C in some

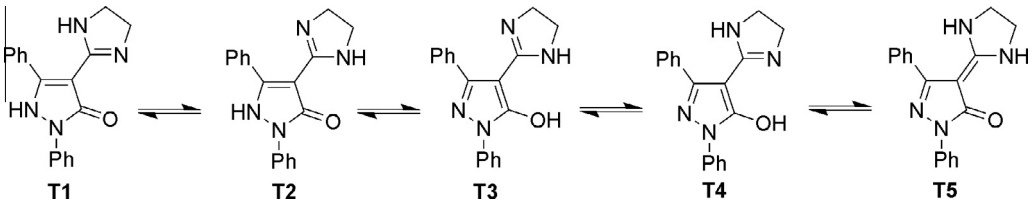


Fig. 7. Various tautomeric form of compound **3e**.

Table 3
Selected bond lengths, bond angles of compound **3d–f** from XRD data.

Compound **3d**		Compound **3e**		Compound **3f**	
Bond distances (Å) with esd's parentheses					
C1–C2	1.525(11)	C1–C10	1.4792(19)	C3–C6	1.495(4)
C2–N2	1.330(10)	C1–N2	1.3187(18)	C3–N2	1.314(4)
C2–C3	1.420(11)	C1–C2	1.4190(19)	C3–C4	1.420(4)
C3–C11	1.380(12)	C2–C16	1.408(2)	C4–C13	1.402(5)
C3–C4	1.391(11)	C2–C3	1.427(2)	C4–C5	1.408(4)
C4–O1	1.276(7)	C3–O1	1.2447(17)	C5–O1	1.267(4)
C4–N1	1.387(10)	C3–N1	1.3947(19)	C5–N1	1.370(4)
C5–N1	1.389(10)	C4–N1	1.4107(18)	C7–N1	1.427(4)
C11–N3	1.316(10)	C16–N4	1.3438(18)	C13–N4	1.346(4)
C11–N4	1.359(9)	C16–N3	1.3187(18)	C13–N3	1.354(4)
N1–N2	1.438(8)	N1–N2	1.3909(16)	N1–N2	1.404(3)
Bond angles (°) with esd's parentheses					
N2–C2–C3	112.7(7)	N2–C1–C2	111.63(12)	N2–C3–C4	111.5(3)
N2–C2–C1	117.1(8)	N2–C1–C10	117.52(12)	N2–C3–C6	118.5(3)
C3–C2–C1	130.2(8)	C2–C1–C10	130.77(13)	C4–C3–C6	130.0(4)
C4–C3–C2	106.0(7)	C1–C2–C3	106.33(12)	C3–C4–C5	106.2(3)
O1–C4–C3	128.7(8)	O1–C3–C2	130.67(13)	O1–C5–C4	130.8(4)
C10–C5–N1	122.4(7)	C9–C4–N1	120.87(13)	C12–C7–N1	119.3(3)
N1–C5–C6	118.3(8)	N1–C4–C5	119.90(14)	N1–C7–C8	120.5(4)
N3–C11–N4	108.4(7)	N3–C16–N4	110.17(12)	N3–C13–N4	109.1(4)
N3–C11–C3	128.7(7)	N4–C16–C2	126.48(12)	N4–C13–C4	128.7(4)
N4–C11–C3	122.9(7)	N3–C16–C2	123.35(13)	N3–C13–C4	122.2(4)

relative compounds, 1.400(2) Å [30] and 1.392(8) Å [33]. From the X-ray data, 1.319(2) Å and 1.344(2) Å, bond distances obtained for C(16)–N(3), C(16)–N(4) respectively are compared with C=N value (1.292 Å) reported by Peng et al. [35]. C(16)–N(3) with 1.319 Å has partial double bond character than the C(16)–N(4), 1.344 Å. Further the bond lengths N(2)–C(1) (1.319 Å) and C(1)–C(2) (1.419 Å) are slightly differ from the normal C=N and C–C bond length. This observation suggests that compound **3e** involve in the tautomerization through the delocalization of electrons around N2–C1–C2–C16–N3 chain. Also from the X-ray structure analysis, pyrazolone ring (C1–N2–N1–C3–C2) and the imidazolyl ring (C16–N3–C18–C17–N4) of **3e** virtually exhibit coplanarity with the dihedral angle (15.18°) and the torsion angle for C1–C2–C16–N3 is 175.85(14)°. These observations reveal that of electronic delocalization about N2–C1–C2–C16–N3 chain and this extends even up to C3 carbon, and not with N4 atom. In addition, the N(3) atom is strongly hydrogen bonded with the O(1) atom, the N(3)···O(1) distances is 2.842 Å and the angle of N(3)–H(3)···O(1) is 126.08°. Therefore, the crystal study shows that the compound exists in the amine-one form.

The geometrical optimizations of compound **3e** and its different tautomeric forms were performed by B3LYP/6-31G** method (Fig. 8 and S2). Total energy and the HOMO, LUMO energies of the all the isomers were assigned and listed in Table 4. HOMO, LUMO diagram of **T1–T5** was also predicted, is shown in Fig. S1. Accordingly, calculated total energy of the tautomer 5 (**T5**) (−620909.36 kcal/mol) is comparably lower than the tautomer 1 (**T1**) (−620882.31 kcal/mol) and the other tautomers (**T2–T4**) energy are lying in between the above two (**T1** & **T5**). Hence **T5** is identified as the stable form of tautomer with 1.1726 eV than **T1**, hence the physical parameters of more reliable form of **T5** is

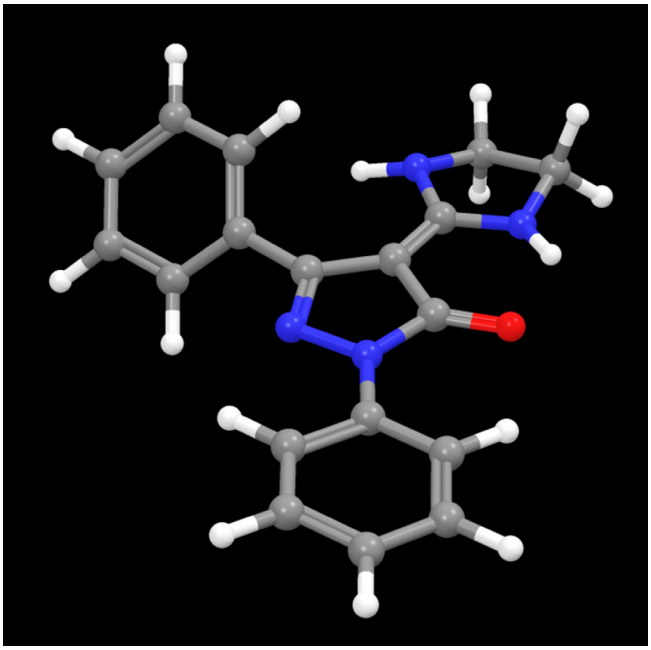


Fig. 8. The B3LYP/6-31G** optimized structure (**T5**) of compound **3e**.

compared with X-ray diffraction data of **3e**. Bond lengths, bond angles and torsion angles obtained from X-ray diffraction study and optimization by B3LYP/6-31G** level study are listed in Tables 5 and S1 (supplementary). Based on the optimization data from Table 5, the single bond distances of N1–N2, C16–N4 and C1–C2 are 1.384 Å, 1.368 Å and 1.430 Å respectively, while the double bond distances of N2–C1, C3–O1 and C2–C16 are 1.315 Å, 1.248 Å and 1.397 Å by B3LYP/6-31G** level which are consistent with XRD structure. But C16–N3 and C16–N4 with bond distances 1.348 Å, 1.368 Å differ from actual by 1.319 Å and 1.344 Å, respectively; suggest that C16–N3 is much involving delocalization with C2–C16 double bond.

Moreover, the bond angles C2–C16–N3, N3–C16–N4, C2–C3–O1 and C2–C1–C10 are 122.0°, 109.0°, 129.1° and 130.3°, respectively are also consistent with actual values of 123.35(13)°, 110.17(12)°, 130.67(13)° and 130.77(13)° respectively. Torsion angles of stable **T5** at C16–C2–C3–O1, C3–C2–C16–N3 are 6.2° and −1.1° also exhibit good agreement with the crystal structure of **3e**. Consequently, we suggest that O1–C3–C2–C16–N3–H3 are lying in a plane, involves the intra molecular hydrogen bonding as well as coplanarity exists in the planes of pyrazolone with C4 heterocycles.

5. Conclusion

A general procedure for the synthesis of heterocycle substituted pyrazolones from the simple starting materials like pyrazolone ketene dithioacetal synthon has been developed. 1,3-azoles/oxazoles and benzannulated azoles/oxazoles are readily constructed on pyrazolone moiety in the absence of any catalyst. All the synthesized

Table 4
Theoretically computed energies for structures **T1–T5.**

S. No.	Parameters	T1	T2	T3	T4	T5
1	HOMO energy (kcal/mol)	−128.94	−123.70	−126.59	−132.42	−115.96
2	LUMO energy (kcal/mol)	−35.39	−38.50	−21.43	−18.31	−21.70
3	Zero point energy (kcal/mol)	195.91	196.52	195.98	196.15	196.84
4	Total energy (kcal/mol)	−620882.31	−620886.85	−620893.03	−620902.59	−620909.36

Table 5
Selected bond distances (Å), bond angles (°) and dihedral angles (°) of **3e** by crystal study with optimization.

Parameters	Experimental XRD	Theoretical B3LYP (**T5**)	Parameters	Experimental XRD	Theoretical B3LYP (**T5**)
N1–N2	1.3909(16)	1.384	C2–C1–C10	130.77(13)	130.3
N2–C1	1.3187(18)	1.315	N2–C1–C10	117.52(12)	118.7
C1–C2	1.4190(19)	1.430	C3–N1–C4	128.47(12)	128.9
C2–C3	1.427(2)	1.451	N2–N1–C4	119.26(11)	118.8
C3–O1	1.2447(17)	1.248	C16–N3–H3	122.8(12)	117.2
C2–C16	1.408(2)	1.397	C3–N1–C4–C5	−22.3(2)	−6.2
C16–N3	1.3187(18)	1.348	N2–N1–C4–C9	−1.28(15)	−3.1
C16–N4	1.3438(18)	1.368	C1–C2–C3–N1	1.73(15)	0.6
C1–C10	1.4792(19)	1.477	C16–C2–C3–O1	8.6(2)	6.2
N1–C4	1.4107(18)	1.416	C3–C2–C16–N3	−1.3(2)	−1.1
N1–C3	1.3947(19)	1.397	C1–C2–C16–N4	−3.8(2)	8.1
N1–N2–C1	105.90(11)	107.3	C10–C1–C2–C16	−11.6(3)	−7.9
C1–C2–C3	106.33(12)	105.6	C10–C1–N2–N1	−178.54(11)	−180.0
C2–C3–O1	130.67(13)	129.1	N2–C1–C10–C15	131.54(15)	138.8
C2–C16–N3	123.35(13)	122.0	N2–C1–C10–C11	−44.67(19)	−38.9
C2–C16–N4	126.48(12)	129.0	C2–C1–C10–C15	−45.1(2)	−41.7
N3–C16–N4	110.17(12)	109.0	N3–C18–C17–N4	4.7(2)	25.6

compounds **3a–i** in the present project were characterized by IR, ^{1}H NMR, ^{13}C NMR, 2D NMR and XRD techniques. Compounds **3d–f** were crystallized as monoclinic system and their structural parameters were evaluated. For compound **3e**, stable form of the tautomer, (**T5**) was identified by the DFT calculation with B3LYP, 6-31G** basis set level and the physical parameters of **T5** were compared with X-ray data, which exhibit good consistency with the proposed structure was obtained.

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Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 904627 (**3d**), CCDC 945144 (**3e**) and CCDC 916999 (**3f**). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033: or e-mail: deposit@ccdc.cam.ac.uk. Frontier orbitals for **T1–T5** of compound **3e** and spectral data of all the compounds **3a–i** are given in supplementary figures **S1–S25**. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.10.018.

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