International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 04 Issue: 09 | Sep -2017 www.irjet.net p-ISSN: 2395-0072

Synthesis, Crystal and Molecular Structure Studies of a new pyrazole compound

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Abstract - *The title molecule $C_{10}H_9N_2O$,(* **3-methyl-**1phenyl-4,5-dihydro-1H-pyrazol-5-one)*categorised under the ménage of pyrazole is acquired and crystallized to obtain crystals suitable for x-ray diffraction at 296K. X-ray diffraction studies established that the compound is crystallized with two independent molecules in its asymmetric unit under primitive monoclinic system in $P2_1/c$ space group. The unit cell parameters are a = 10.2163(4) Å , b = 11.1084(4) Å, c = 15.6924(6)Å , and β= 95.441(1)° with Z=8. The R-factor converged to 0.0426 for 2907 reflections. The pyrazole ring in each molecule is wrapped by a phenyl ring, a methyl group and a keto group. The crystal packing is mainly due to inter molecular hydrogen bonds of type C-H... O and the C-H...π bonds linking the molecules. The bond length, bond angles, torsion angles and plane orientations of the moieties in the molecule are discussed.*

Key Words: **X-ray, hydrogen bond, monoclinic, pyrazole, crystal structure**

1. INTRODUCTION

Pyrazole , also known as azole is identified to be an heterocyclic compound wrapped by three carbon atoms and two adjacent nitrogen atoms.[1]Heterocyclic compounds are generally known for their significance in the pharmaceutical industry in line with new drug development, with more than 50% of the drugs and organic compounds holding these compounds as one of its substituents.[2] Molecules containing core pyrazole unit is of great demand in various fields like medicinal chemistry, pharmacy , agro-chemical industries and even more [3]. The compound that caught the attention of scientists are synthesized and discussed for various astonishing properties. These synthesized pyrazoles when altered with different substituents, can do wonders with overwhelming biological activities like anti-bacterial [4], anti-inflammatory [5], anti-tumor [6], anti-fungal [7], anti-microbial [8], anti-cancer [9] etc., These pyrazole containing derivatives also find application as insecticides [10] and herbicides[11] in agrochemical industry. Substituted pyrazoles are reported to possess some important photophysical properties that can be employed in organic light-emitting diode fabrication [12] and also as fluorescent agents [13].

Keeping in mind, the multifarious activities of this heterocyclic scaffold we herein report the synthesis and characterization of the title compound.

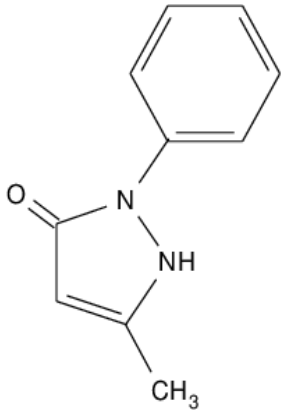

Figure - : Schematic diagram of the molecule

2. MATERIALS AND METHODS

2.1 Synthesis and Crystallization:

The title compound was synthesized as per the procedure described earlier [14]. Ethyl aceto acetate (0.1mol) and (0.1 mol) phenyl hydrazine is mixed together in a large evaporating dish .The mixture is then heated on a boiling water bath in the fume cupboard for about 2 hrs while stirring continuously. The obtained heavy reddish syrup is allowed to cool for a while and 200ml of ether is added to it. The solidified mixture is then filtered and washed thoroughly with ether to remove colored impurity and is recrystallized from hot water.

2.2 Data Collection

The colorless single crystal block of the title compound whose dimensions are 0.25 x 0.26 x 0.28 mm is subjected for

an X-ray diffraction study. X-ray intensity data were collected for the title compound at temperature 296K on a Bruker X8 Proteum diffracto- meter using CuKα radiation of wavelength 1.54178 Å. X-ray diffraction studies revealed that the compound is crystallized in primitive monoclinic crystal system in $P2_1/c$ space group. Complete data set is processed using *SAINT* [15]. The structure is solved by direct methods and refined by full-matrix least squares method on F^2 using *SHELXS -97* and *SHELXL-97*[16] programs. All the non-hydrogen atoms were revealed in the first difference fourier map itself. After several cycles of refinement, the final difference fourier map showed peaks of no chemical significance and the residual is saturated. The geometrical calculations were carried out using the program *PLATON*.The details of the crystal structure and data refinement are given in Table 1. The list of bond lengths and bond angles of the non-hydrogen atoms are given in Table 2 and 3. Figure- 2 represents the ORTEP of the molecule with thermal ellipsoids drawn at 50% probability.

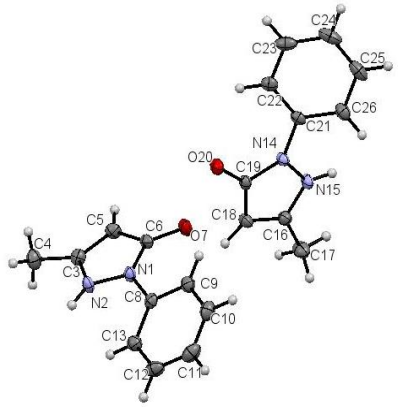

Figure – 2 : ORTEP diagram of the molecule (Drawn at 50% probability level)

2.3 Results and Discussion

Bond lengths and bond angles listed in Table-2 and Table-3 abides well with the standard values and is comparable to 5-Ethyl-4-phenyl-1*H*-pyrazol-3(2*H*)-one [17]. The molecule is almost planar with 2 independent molecules in its asymmetric unit. The central pyrazole core in each molecule is encased by a phenyl ring, a methyl group and a keto group. The pyrazole ring is affected by π conjugation which is confirmed by the aberration observed in the bond length that form the ring structure 1.387(2)Å of N1-N2, 1.351(2) Å of N2-C3, 1.368(2)Å of C3-C5, 1.411(2) Å of C5-C6, 1.385(2) Å of C6-N1 . Likewise, The fluctuations in the bond length 1.486(2)Å of (C3-C4) and 1.492(2) Å of (C16-C17) of the methyl group from the standard value is attributed to sp^3 hybridization.

The dihedral angle between the pyrazole ring (N1/N2-C3-C5-C6) and the attached phenyl ring (C8-C13) is 22.04(19)° for one of the molecule whereas the dihedral angle between the pyrazole ring (N14/N15-C16-C18-C19) and the attached phenyl ring (C21-C26) is 32.21(9)° for the other. The bond length 1.266(2) Å of C6-O7and 1.328(2) Å of C19-O20 shows double-bond character which can be attributed to the formation of keto group. The methyl groups in both the molecule lies in the plane of the pyrazole ring . The C=O group in both the molecules adopts *+antiperiplanar conformation (+ap) as* indicated by the torsion angle 178.5(2)° for the atoms (O7-C6-C5-C3) and 179.6(2)° for the atoms (O20-C18-C19-C16) correspondingly. The structure exhibits intermolecular hydrogen bonds of the type C-H…O shown by C24-H12…O20 with length of 3.480(2) Å and an angle of 159° whose symmetry codes are [-x, 1/ 2+y, 1/2-z].The molecule is also stabilized by the C-H…π interactions.

Table – 1: Crystal data and structure refinement table

Empirical Formula	$C_{10}H_9N_2O$
Formula Weight	173.19
Temperature	296 K
Wavelength	1.54178 Å
Crystal System	Monoclinic
Space group	$P2_1/c$
Cell dimensions	a = 10.2163(4) Å b = 11.1084(4) Å c = 15.6924(6) Å β = 95.441(1)°
Volume	1772.86(12) $Å^3$
Z	8
Density	1.298 g/cm^3
F_{000}	728
Crystal Size	0.25 x 0.26 x 0.28 mm
Theta range for data collection	4.3° to 64.4 °
Index ranges	-11 ≤ h ≤ 11 -11 ≤ k ≤ 12 -18 ≤ l ≤ 17
Independent reflections	2907 [R(int) =0.039]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2907 / 00 /237
Goodness-of-fit on F^2	1.07
Final R indices [I > 2σ (I)]	R1 = 0.0426, ωR2 = 0.1145
Largest diff. peak and hole	-0.23 e. $Å^{-3}$ and 0.82 e. $Å^{-3}$

Table – 2: Bond Lengths [Å] for Non-Hydrogen atoms

Atoms	Length	Atoms	Length
O7-C6	1.265(2)	C6-C5	1.411(2)
O20-C19	1.325(1)	C3-C5	1.368(2)
N1-N2	1.383(1)	C3-C4	1.486(2)
N1-C6	1.387(2)	C21-C22	1.391(2)
N1-C8	1.418(2)	C16-C18	1.406(2)
N2-C3	1.346(2)	C16-C17	1.492(2)
N14-C19	1.365(2)	C18-C19	1.379(2)
N14-N15	1.378(1)	N15-C16	1.327(2)
N14-C21	1.420(2)		

Table – 3: Bond Angels [°] for Non-Hydrogen atoms

Atoms	Angle	Atoms	Angle
N2-N1-C6	108.5(1)	O7-C6-N1	122.0(1)
N2-N1-C8	120.4(1)	O7-C6-C5	132.0(1)
C6-N1-C8	129.9(1)	N1-C6-C5	105.8(1)
C3-N2-N1	108.1(1)	C3-C5-C6	107.8(1)
C19-N14-	110.3(1)	C22-C21-N14	120.6(1)
C19-N14-	129.8(1)	C26-C21-N14	118.8(1)
N15-N14-	119.7(1)	N15-C16-C18	111.0(1)
C16-N15-	105.8(1)	N15-C16-C17	120.2(1)
C13-C8-N1	119.7(1)	C18-C16-C17	128.7(1)
C9-C8-N1	120.0(1)	C19-C18-C16	105.5(1)
N2-C3-C5	109.3(1)	O20-C19-N14	120.0(1)
N2-C3-C4	119.6(1)	O20-C19-C18	132.7(1)
C5-C3-C4	131.0(1)	N14-C19-C18	107.2(1)

Table – 4: Torsion Angels [°] for Non-Hydrogen atoms

Atoms	Torsions	Atoms	Torsions
C10 -C11 -C12 -C13	0.7(3)	C21 -N14 -N15 -C16	179.8(1)
C12 -C11 -C10 -C9	0.4(3)	C19 -N14 -N15 -C16	-0.1(2)
C11 -C12 -C13 -C8	-1.4(3)	N15 -N14 -C19 -O20	-179.7(1)
C8 -N1 -N2 -C3	-173.8(1)	N15 -N14 -C19 -C18	0.6(2)
N2 -N1- C6 -O7	-176.3(1)	C21- N14 -C19 -O20	0.4(2)
N2 -N1 -C6 -C5	2.8(2)	C21 -N14 -C19 -C18	-179.4(1)
C8 -N1 -C6 -O7	-8.0(2)	N14 -N15 -C16 -C17	178.0(1)
C8- N1 -C6 -C5	171.2(1)	N14 -N15 -C16 -C18	-0.4(2)
N1 -N2 -C3 -C4	-176.9(1)	C23 -C24 -C25 -C26	0.3(3)
N1- N2 -C3 -C5	3.7(2)	C25 -C24 -C23 -C22	-1.6(3)
C12- C13- C8- N1	-178.5(1)	C24 -C25 -C26 -C21	1.6(2)
C12 -C13 -C8 C9	1.1(2)	C25 -C26 -C21 -N14	176.1(1)
N1 -C8 -C9 -C10	179.6(1)	N14 -C21 -C22 -C23	-177.3(1)
C13 -C8 -C9 -C10	-0.0(2)	C26 -C21 -C22 -C23	1.1(2)
N2 -C3- C5 -C6	-2.0(2)	N15 -C16 -C18 -C19	0.7(2)
C4 -C3 -C5 -C6	178.8(2)	C17 -C16 -C18 -C19	-177.5(2)
C11 -C10- C9- C8	-0.7(3)	C24 -C23- C22 -C21	0.9(2)
O7 -C6 -C5 -C3	178.5(2)	C16 -C18 -C19 -O20	179.6(2)
		C16 -C18 -C19 -N14	-0.7(2)

Table – 4: Hydrogen bond geometry [Å and °]

D-H…A	D-H(Å)	H…A(Å)	D…A(Å)	DHA(°)
C9-H4…O7	0.93	2.37	2.920(2)	118
C24-H12…O20 (i)	0.93	2.60	3.480(2)	159
C22-H20…O20	0.93	2.43	2.930(2)	114

Symmetry codes: [-x, 1/ 2+y, 1/2-z]

3. CONCLUSIONS

The essentiality of the heterocyclic compounds in pharmaceutical industry, medicinal chemistry, pesticide chemistry, agrochemical industry etc., has heightened for the reason that it displays favorable biological features. Usually, the compounds like pyrazole framed out of this heterocyclic skeleton exhibit variegated biological activities like anti-microbial, antimalarial, antitubercular, anticancer, anti-inflammatory, antidepressant, antitumour, and antihistaminic agents. This paper reveals the synthesis and characterization of 3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-5-one a new pyrazole compound. The structure details are obtained using single crystal X-ray diffraction studies and optimized geometrical parameters are close to the experimental bond lengths and angles.

ACKNOWLEDGEMENT

The authors thank the Institution of Excellence, Vijnana Bhavana, University of Mysore, Mysuru for providing the Single-crystal X-ray diffractometer facility.

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