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Crystal and Molecular Structure Studies of 1-(5-(4-chlorophenoxy)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-N-(4-chlorophenyl)methanimine

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Abstract - *The title molecule $C_{23}H_{16}Cl_2N_3O$ which belongs to the family of pyrazole is procured and crystallized to obtain crystals suitable for x-ray diffraction at 293k. X-ray diffraction studies exposed that the compound has been crystallized in primitive monoclinic system in $P2_1/n$ space group. The unit cell parameters are a = 10.7220(4) Å, b = 18.1623(7) Å, c = 11.1084(4) Å, and β= 109.910(2) ˚with Z=4. The R-factor converged to 0.047 for 3354 reflections. The phenyl, chlorophenyl and the chlorophenoxy rings are angled to the pyrazole ring stationed in the center of the molecule at 35.60(1)° , 36.57(1)° and 70.55(1)° respectively. The crystal packing is stabilized by inter molecular hydrogen bonds of type C-H…Cl and the pairs of C-H…π bonds link 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, a heterocyclic diazole classified under alkaloid is characterized by a 5-membered ring with three carbon atoms and two adjacent nitrogen atoms. [1] Although found rarely in nature, synthesized pyrazole derivatives treasures distended application in the field of medicine, medicinal chemistry,[2] agriculture and pesticide chemistry. Pyrazole moiety is found in many dyes, drugs and even as synthetic scaffolds for the construction of bioactive molecules. [3] Substituted derivatives of pyrazole are important biological agents. These are used as anti-bacterial [4], anti-histamic [5], anti-inflammatory [6], analgesic [7], anti-tumor [8], anti-fungal [9], anti-microbial [10], anti-cancer [11], anti-glaucoma. Due to its voluminous range of biological activity, pyrazoles establishes a relevant synthetic route in pharmaceutical industry where they represent the core structure for number of drugs. Additionally, organic molecules based with pyrazole ring are utilized in agro-chemical industries. In view of the above said facts we herein report the synthesis and characterization of the title compound.

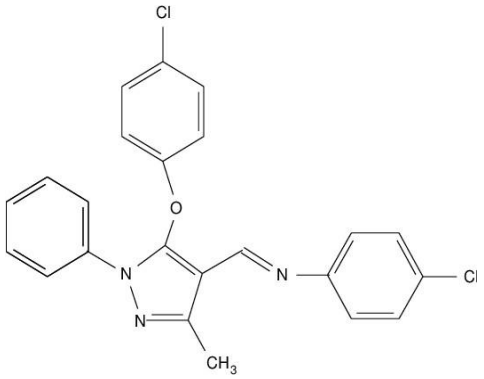

Figure - : Schematic diagram of the molecule

2. MATERIALS AND METHODS

2.1 Synthesis and Crystallization:

The title compound was synthesized as per the procedure described earlier [12]. 5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-carboxaldehyde (0.1 mol) and N-methyl piperizine (0.1mol) was dissolved in 10ml of dimethyl sulfoxide. To this solution (0.1mol) of potassium hydroxide was added, the reaction mixture is heated in an oil bath maintained at 60°c for 6 hrs. The mixture is poured into crushed ice. The solid obtained was recrystallized from suitable solvent.

2.2 Data Collection

The colorless single crystal block of the title compound whose dimensions are 0.24 x 0.26x 0.28 mm is subjected for an X-ray diffraction study. X-ray intensity data were collected for the title compound at temperature 293K on a Bruker X8 Proteum diffractometer using CuKα radiation of wavelength 1.54178 Å. X-ray diffraction studies revealed that the compound is crystallized in primitive monoclinic crystal system in $P2_1/n$ space group. Complete data set is processed using *SAINT* [13]. The structure is solved by direct methods and refined by full-matrix least squares method on F^2 using *SHELXS -97* and *SHELXL-97*[14] 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 molecular and packing diagrams were generated using the software *MERCURY*. 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.

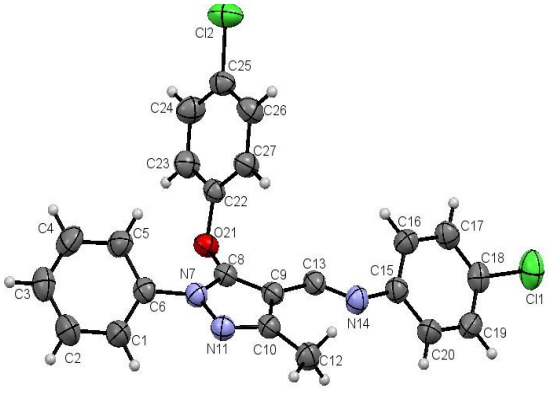

Figure – 2 : ORTEP diagram of the molecule (Drawn at 50% probability level)

2.3 Results and Discussion

Bond lengths and bond angles listed in Table-2 and Table-3 commensurate well with the standard values and is comparable to 5-(4-Chlorophenoxy)-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde[15]. The molecule is almost planar with the pyrazole ring hedged by a phenyl ring, chlorophenyl and chlorophenoxy rings. Variations observed in the bond lengths that frame up the pyrazole ring 1.383(3)Å of N11-N7, 1.350(3)Å of N7-C8, 1.372(4)Å of C8-C9, 1.426(4)Å of C9-C10, 1.329(3)Å of C10-N11 from the normal range is attributed to π conjugation. Also, deviations in the bond length 1.485(4) Å of C10-C12 of the methyl group from the standard value is associated with sp^3 hybridization.

The displacement in the location of the oxygen atom that bridges the pyrazole ring and chlorophenyl ring from the pyrazole plane is confirmed by the deviations inspected in the bond angle 130.4(2)° of O21-C8-C9. The pyrazole ring (N7/N11/C8/C9/C10) makes dihedral angle of 35.60(1)° with the phenyl ring (C1-C6) and 36.57(1)° with the chlorophenyl ring (Cl1/C15-C20) and 70.55(1)° with the chlorophenoxy ring (Cl2/C22-C27). The methyl group which lies in the pyrazole plane adopts *-anti periplanar conformation(-ap)* with respect to the pyrazole plane as confirmed by the torsion angle -178.1(3)° for the atoms C8-C9-C10-C12. The structure exhibits intermolecular hydrogen bonds of the type C-H…Cl shown by C24-H24A**…**Cl1 with length of 3.628(3) Å and an angle of 150° whose symmetry codes are [-x,-y,1-z]. The molecule is also stabilized by the C-H…π interactions.

Table – 1: Crystal data and structure refinement table

Empirical Formula	$C_{23}H_{16}Cl_2N_3O$
Formula Weight	421.29
Temperature	293 K
Wavelength	1.54178 Å
Crystal System	Monoclinic
Space group	P21/n
Cell dimensions	a = 10.7220(4) Å
	b = 18.1623(7) Å
	c = 11.1466(4) Å
	β = 109.910(2)°
Volume	2040.90(13) $Å^3$
Z	4
Density	1.371 g/cm^3
F_{000}	868
Crystal Size	0.25 x 0.26 x 0.28 mm
Theta range for data collection	5.5° to 64.4°
Index ranges	-12 ≤ h ≤ 12
	-19 ≤ k ≤ 21
	-12 ≤ l ≤ 13
Independent reflections	3354 [R(int) = 0.058]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3354 / 00 /263
Goodness-of-fit on F^2	1.06
Final R indices [I > 2σ (I)]	R1 = 0.0477, ωR2 = 0.1451
Largest diff. peak and hole	-0.37 e.$Å^{-3}$and 0.57 e.$Å^{-3}$

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

Atoms	Length	Atoms	Length
Cl1-C18	1.741(3)	C10-C12	1.485(4)
Cl2-C25	1.735(3)	C13-N14	1.261(3)
C6-N7	1.424(3)	N14-C15	1.411(4)
N7-C8	1.350(3)	O21-C22	1.398(3)
N7-N11	1.383(3)	C9-C10	1.426(4)
C8-O21	1.362(3)	C9-C13	1.452(4)
C8-C9	1.372(4)	C10-N11	1.329(3)

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

Atoms	Angle	Atoms	Angle
C1-C6-N7	119.0(2)	C13-N14-C15	120.0(2)
C5-C6-N7	121.3(2)	C16-C15-N14	124.6(3)
C8-N7-C6	130.1(2)	C20-C15-N14	116.5(2)
N11-N7-C6	119.4(2)	C19-C18-Cl1	118.5(2)
N7-C8-O21	120.4(2)	C17-C18-Cl1	119.8(2)
N7-C8-C9	108.9(2)	C8-O21-C22	120.1(1)
O21-C8-C9	130.4(2)	C23-C22-O21	115.0(2)
C8-C9-C13	125.7(2)	C27-C22-O21	123.8(2)
C10-C9-C13	130.1(2)	C26-C25-Cl2	119.6(2)
N11-C10-C12	119.7(2)	C24-C25-Cl2	119.6(2)
C9-C10-C12	129.1(2)	C10-N11-N7	105.6(2)

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

Atoms	Torsions	Atoms	Torsions
C2 -C1- C6 -N7	179.3(3)	C12- C10- N11- N7	177.7(2)
C1 -C2 -C3 -C4	-1.1(5)	C9 -C13- N14 -C15	178.7(2)
C4 -C5 -C6 -N7	179.1(3)	N14 -C15 -C16 -C17	177.6(3)
C1 -C6 -N7- C8	140.5(3)	N14 -C15 -C20 -C19	-178.6(3)
C6- N7 -C8- C9	-174.9(2)	C16 -C17 -C18 -Cl1	-178.3(2)
C6 -N7- C8 -O21	-0.5(4)	Cl1 -C18 -C19 -C20	177.7(2)
N11 -N7 -C8 -O21	173.4(2)	C18 -C19- C20 -C15	1.2(5)
N7 -C8 -C9- C10	0.3(3)	O21- C22- C23- C24	178.1(3)
O21- C8- C9- C10	-173.5(2)	O21 -C22 -C27 -C26	-178.5(2)
C9 -C8 -O21 -C22	-79.0(3)	C23 -C24- C25 -Cl2	-177.2(2)
C13- C9- C10- N11	-175.9(2)	C24 -C25 -C26 -C27	-1.0(5)

Table – 5: Hydrogen bond geometry [Å and °]

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	DHA(°)
C24-H24A...Cl1	0.93	2.79	3.628(3)	150

Symmetry codes: [–x, -y, 1-z]

3. CONCLUSIONS

Heterocyclic compounds are in great demand nowadays for their excellent properties that plays vital role in medicinal industry and agricultural industry. Generally, the structures of those compounds that are built with heterocyclic systems illustrate diverse biological activities. Reports reveal the striking participation of synthesized pyrazoles in as many as biological and pharmaceutical activities like anti-microbial, antimalarial, antitubercular, anticancer, anti-inflammatory, antidepressant and antihistaminic agents. This paper reveals the synthesis and characterization of 1-(5-(4-chlorophenoxy)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-N- (4-chloro phenyl)methanimine 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.

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