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SYNTHESIS AND CRYSTAL STRUCTURE ANALYSIS OF 4-(2-(4-CHLORO-PHENYL)-4,5-DIPHENYL-1*H*-IMIDAZOLE-1-YL)-2,3-DIMETHYL-1-PHENYL-1,2-DIHYDROPYRZOL-5-ONE

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ABSTRACT

The title compound, 4-(2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole-1-yl)-2,3-dimethyl-1-phenyl-1,2-dihydropyrzol-5-one ($C_{32}H_{25}ClN_4O$), crystallizes in the monoclinic crystal system with space group $P2_1/c$ with unit cell parameters: a = 7.7847(7) Å, b = 17.5077(14) Å, c = 19.8332(19) Å, β = 92.783(8)° and Z = 4. The crystal structure has been solved by using direct methods and refined by full matrix least-squares procédures to a final R-factor of 0.085 for 1944 observed reflections. In the crystal structure, molecules are linked by C–H···O intermolecular hydrogen bonds, forming chains along b-axis. The structure also exhibits C–H···π interaction and intramolecular H-bonds of the type C–H···N.

Keywords: Crystal Structure, Imidazole, Pyrazole, Direct Methods, Intermolecular interaction.

INTRODUCTION

Imidazole and pyrazole scaffolds display improved efficacy and show potential *antibacterial* and *antifungal* activities[1]. Imidazole and its derivatives have a long history of applications in the agrochemical and pharmaceutical industry. These systems possess a wide spectrum of pharmacological activities such as *anti-convulsant*[2], *antitubercular*[3], *anti-inflammatory*[4], *antimicrobial*[5], *anticancer* and *anti-Parkinson*[6]. Pyrazole is well established in the literature as important biologically active heterocyclic compounds due to their widespread potential biological and pharmacological activities[7]. They have shown significant biological activities, such as *anti-microbial*[8], *analgesic*[9], *anti-inflammatory*[10] and *anticancer*[11] activities and in view of these pertinent features that we got interested in the synthesis and structure analysis of 4-(2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole-1-yl)-2,3-dimethyl-1-phenyl-1,2-dihydropyrzol-5-one.

EXPERIMENTAL

Synthesis

A mixture of benzil (0.210 g, 1.0 mmol), 4-Aminoantipyrine (0.203 g, 1.0 mmol), 4-Chlorobenzaldehyde (0.140 g, 1.0 mmol), ammonium acetate (0.077g, 1.0 mmol) and ZnO nanoparticles (0.008 g, 0.1 mmol) in glacial acetic acid (15 mL) was stirred for 3 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. The reaction mixture was then poured into cold water. The solid separated was filtered by suction to afford crude product. The pure product was obtained by further recrystallization from ethanol. Single crystal of the purified product was developed from acetone by a slow evaporation method (M.P.: 483-485K). The reaction scheme of the compound is given in Fig.-1.

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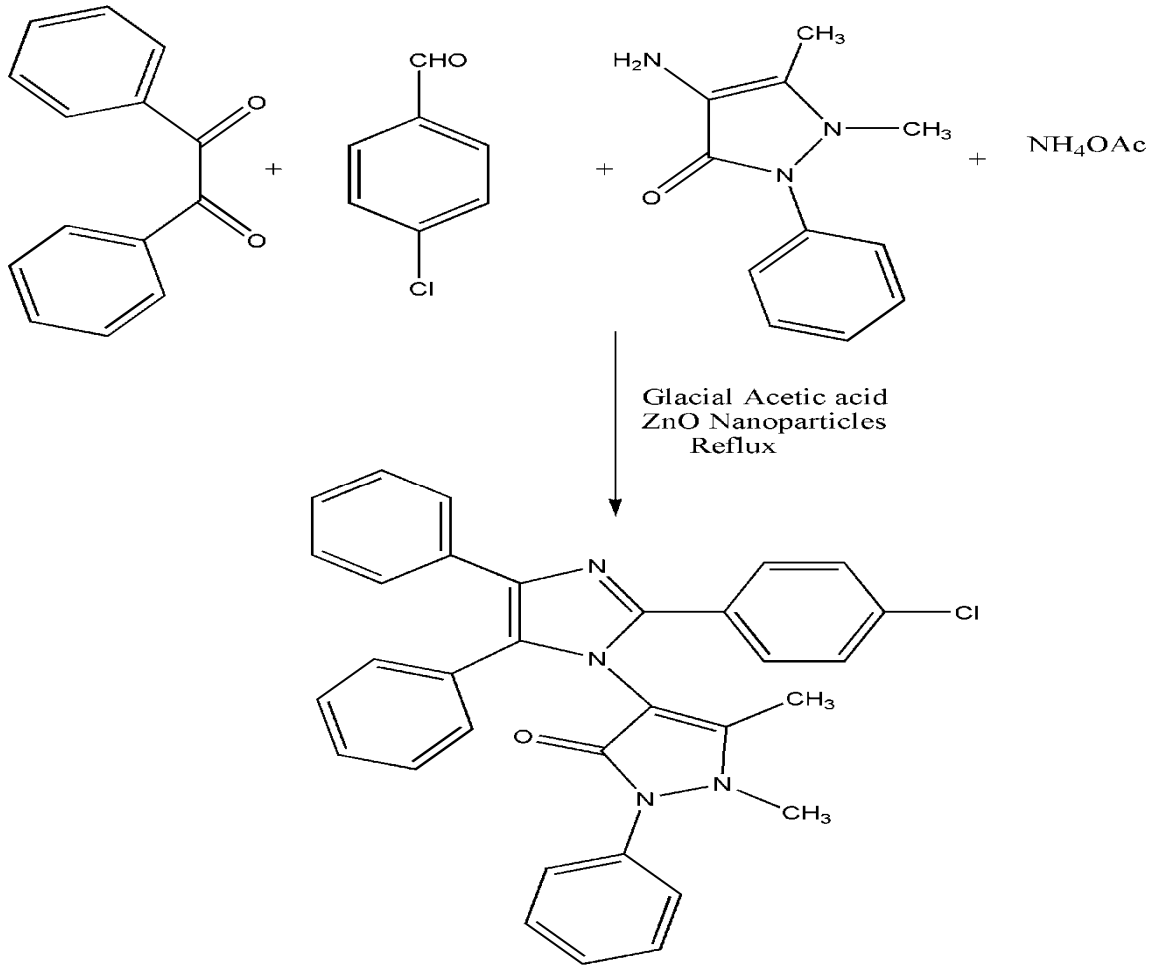

Fig.-1: Reaction Scheme for the Preparation of 4-(2-(4-Chlorophenyl)-4,5-Diphenyl-1*H*-imidazol-1-yl)-2,3-dimethyl-1-phenyl-1,2-dihydropyrzol-5-one.

Crystal Structure Determination

X-ray intensity data of the crystal of dimensions 0.30 X 0.20 X 0.20 mm^3 was collected on *X'calibur* CCD area-detector diffractometer equipped with graphite monochromated Mo*Kα* radiation (λ = 0.710 Å). X-ray intensity data of 9883 reflections were collected at 293(2) K and out of these reflections 4705 were found unique. The intensities were measured by ω scan mode for θ ranges 3.5° to 25°. 1944 reflections with I>2σ (I) were treated as observed. Data were corrected for Lorentz-polarization and absorption factors. The structure was solved by direct methods using SHELXS97[12] and was refined using SHELXL97[12]. All non-hydrogen atoms of the molecule were located from the best E-map. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding carbon with C-H = 0.93-0.97Å. The final refinement cycles converged to an R-factor of 0.085 and *w*R(F^2) = 0.1863 for 1944 observed reflections. Residual electron densities range from -0.28 to 0.27 e$Å^{-3}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables- 4.2.6.8 and 6.1.1.4). The Geometry of the molecule was calculated using the WinGX[13], PARST[14] and PLATON[15] software.

Crystallographic information has been deposited at the Cambridge Crystallographic Data Centre with CCDC number 1507484. The crystallographic and refinement data of the crystal is given in Table-1.

RESULTS AND DISCUSSION

The molecular structure containing atomic labeling is shown in Fig.-2 (ORTEP)[16]. The molecular structure consists of three phenyls, one chlorophenyl, one imidazole and one pyrazole rings. All the rings, as such, are planar. Bond distances, bond angles and torsion angles which play an important role in

collating the structural properties of this molecule are presented in Table-2. The bond distances and bond angles of all the four six-membered rings show a normal geometry[17]. The C-N bond distances are comparable with the values observed for some analogous structures[18,19]. The N3-N4 distance of 1.385(5)Å is significantly larger than the standard value of 1.350 Å. The deviation in the values of bond angles C25-C24-N4 [122.4(4)º] and C24-N4-C32 [125.9(4)º] is partially due to the torsion present along with the C24-N4 bond (torsion angle C25-C24-N4-C32= 14.4º). The chlorophenyl ring makes a dihedral angle of 40.65° and 84.03° with the imidazole and pyrazole rings, respectively. The phenyl rings (A & B) are twisted by 72.36° and 11.26º, respectively, with respect to the imidazole ring. The pyrazole ring is held almost right angle to the imidazole ring as indicated by the dihedral angle being 89.46°.

In the crystal structure, there exists one intramolecular interaction [C13-H13…N1] and an intermolecular hydrogen bond [C16-H16…O1] that links the molecules into chains along b-axis [Fig.-3 (Mercury)][20]. The details of intra/inter-molecular hydrogen bonds are given in Table-3. The C-H…π contacts as observed in the molecular packing are given in Table-4.

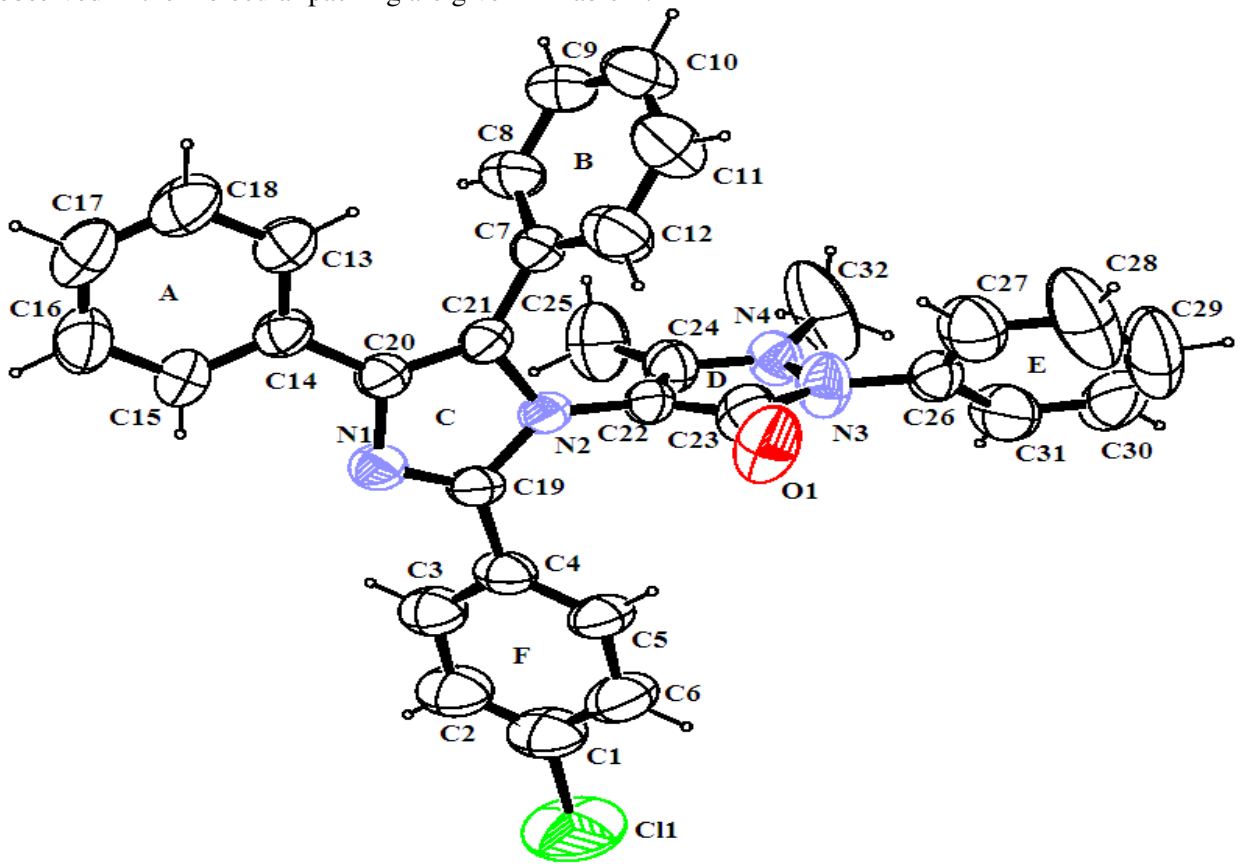

Fig.-2:ORTEP View of the Molecule at a 40% Displacement Ellipsoid Probability Level along with the Atomic Labeling Scheme. Hydrogen Atoms are Drawn at Arbitrary Radii.

Table-1: Crystal and Structure-Refinement Data for $C_{32}H_{25}ClN_4O$.

CCDC Number	1507484
System, Space group, Z	Monoclinic, P $2_1/c$, 4
a, *b*, *c* (Å)	7.7847(7), 17.5077(14), 19.8332(19)
β (°)	92.783(8)
V(Å^3)	2699.9(4)
D_x g.cm^{-3}	1.272
Radiation, λ, Å	0.71073
μ, mm^{-1}	0.174

T, K	293(2)
Sample size, mm^3	0.30 x 0.20 x 0.20
Diffractometer	X'*calibur* Sapphire3 CCD area-detector
Scan mode	ω scan
T_{min}, T_{max}	0.79244, 1.00000
θ range, deg	3.50 to 24.99
h, k, l ranges	*h* = -8 to 9, *k* = -17 to 20, *l* = -23 to 23
Reflections total/unique	9883/4705
Reflections observed [$I > 2\sigma(I)$]	1944
R_{int}	0.103
F(000)	1080
R	0.0853
$wR[F^2]$	0.1863
$(\Delta/\sigma)_{max}$	0.017
Number of refined parameters	346
S	0.924
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.27, -0.28
Programs	SHELXS97[12], SHELXL97[12], PARST[14], PLATON[15], ORTEP[16], MERCURY[20]

Table-2: Selected Bond Distances, Bond Angles and Torsion Angles.

Bond Distances(Å)		Bond Distances(Å)	
C2-C1	1.378 (7)	C21-C20	1.371 (5)
C2-C3	1.400 (6)	C22-C23	1.418 (6)
C4-C3	1.387 (6)	C22-C24	1.341 (6)
C4-C5	1.379 (6)	C25-C24	1.481 (6)
C5-C6	1.391 (6)	C27-C26	1.365 (7)
C6-C1	1.369 (7)	C27-C28	1.376 (8)
C8-C7	1.379 (6)	C28-C29	1.359 (12)
C8-C9	1.387 (6)	C30-C29	1.334 (11)
C9-C10	1.361 (7)	C31-C26	1.364 (6)
C11-C10	1.377 (7)	C31-C30	1.392 (9)
C11-C12	1.392 (6)	C32-N4	1.403 (5)
C12-C7	1.380 (6)	Cl1-C1	1.738 (5)
C14-C13	1.378 (5)	N1-C20	1.390 (5)
C14-C15	1.396 (5)	N2-C19	1.381 (4)
C14-C20	1.472 (5)	N2-C21	1.395 (5)
C16-C15	1.389 (6)	N2-C22	1.423 (4)
C16-C17	1.365 (6)	N3-C23	1.401 (5)
C18-C13	1.389 (6)	N3-C26	1.425 (5)
C18-C17	1.376 (7)	N3-N4	1.385 (5)
C19-C4	1.469 (5)	N4-C24	1.360 (5)
C19-N1	1.326 (4)	O1-C23	1.234 (5)
C21-C7	1.474 (5)		

Bond Angles(°)		Bond Angles(°)	
C2-C1-Cl1	119.4 (5)	N1-C20-C14	119.3 (3)
C6-C1-Cl1	119.2 (5)	C20-C21-N2	105.9 (3)
C20-C21-C7	134.3 (4)	N2-C21-C7	119.8 (3)
C3-C4-C19	121.6 (4)	C24-C22-C23	109.9 (3)
C23-C22-N2	123.7 (4)	C24-C22-N2	125.4 (4)

C5-C4-C19	118.2 (4)	N3-C23-C22	103.5 (4)
C23-N3-C26	126.7 (4)	O1-C23-C22	132.2 (4)
C21-N2-C22	124.0 (3)	O1-C23-N3	124.2 (4)
C8-C7-C21	121.0 (4)	C22-C24-C25	128.1 (4)
C12-C7-C8	117.7 (4)	C22-C24-N4	109.5 (4)
C12-C7-C21	121.3 (4)	N4-C24-C25	122.4 (4)
C13-C14-C20	119.6 (4)	C27-C26-N3	117.9 (4)
C19-N2-C21	106.9 (3)	C31-C26-C27	120.8 (5)
C19-N2-C22	128.5 (3)	C31-C26-N3	121.3 (5)
N1-C19-C4	124.4 (3)	N4-N3-C23	109.9 (3)
C15-C14-C20	122.5 (3)	C19-N1-C20	106.1 (3)
N1-C19-N2	111.0 (3)	N4-N3-C26	123.0 (3)
N2-C19-C4	124.6 (3)	C24-N4-C32	125.9 (4)
C21-C20-C14	130.6 (4)	C24-N4-N3	107.0 (3)
C21-C20-N1	110.1 (3)	N3-N4-C32	124.9 (3)

Torsion Angles(°)		Torsion Angles(°)	
N2-C22-C23-N3	-172.8 (4)	N2-C22-C23-O1	9.7 (9)
N2-C22-C24-N4	173.4 (4)	N2-C22-C24-C25	-7.9 (8)
C22-N2-C19-N1	-171.6 (4)	C22-N2-C19-C4	7.6 (7)
C13-C14-C20-N1	-12.1 (6)	C22-N2-C21-C7	-6.1 (6)
C15-C14-C20-C21	-9.2 (7)	C22-N2-C21-C20	172.4 (4)
C15-C14-C20-N1	168.2 (4)	C19-N2-C22-C23	-102.5 (5)
C21-N2-C22-C23	88.2 (5)	C19-N2-C22-C24	89.4 (6)
C26-N3-C23-C22	174.9 (4)	C21-N2-C22-C24	-79.9 (6)
N1-C19-C4-C3	-137.9 (4)	C26-N3-C23-O1	-7.3 (8)
N1-C19-C4-C5	38.5 (7)	N2-C19-C4-C3	43.0 (7)
N2-C19-C4-C5	-140.6 (4)	C23-N3-C26-C27	-48.3 (7)
C13-C14-C20-C21	170.5 (5)	C23-N3-C26-C31	132.0 (5)
C32-N4-C24-C25	14.4 (8)	N4-N3-C26-C27	124.6 (5)
C20-C21-C7-C8	109.8 (6)	N4-N3-C26-C31	-55.1 (6)
C20-C21-C7-C12	-71.8 (6)	C32-N4-C24-C25	14.4 (8)
N2-C21-C7-C8	-72.1 (6)	C23-N3-N4-C32	165.1 (5)
N2-C21-C7-C12	106.3 (5)	C26-N3-N4-C24	-173.0 (4)
C7-C21-C20-C14	-5.3 (8)	C26-N3-N4-C32	-8.9 (8)

Table-3: Hydrogen Bonding Geometry (e.s.d.`s in Parentheses)

D–H...A	D–H(Å)	H...A(Å)	D...A(Å)	D–H...A(º)
C13-H13... N1	0.93	2.50	2.8441(3)	102
C16-H16...O1^{i}	0.93	2.45	3.3722(3)	171

Symmetry code: (i) -x, 1/2 + y, 1/2 – z

Table-4: Geometry of C-H...π Interaction*

D–H...Cg	D–H(Å)	H...Cg(Å)	D...Cg (Å)	D–H...Cg (º)
C32-H32A...Cg1^{i}	0.93	2.80	3.6485(3)	147

Symmetry code: (i) 1+x, y, z

* Cg1 represent the center of gravity of imidazole(C) ring.

CONCLUSION

The structure of 4-(2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole-1-yl)-2,3-dimethyl-1-phenyl-1,2-dihydropyrzol-5-one consists of six rings, four are bonded to the central imidazole ring and one phenyl to the pyrazole ring. All the rings are almost planar. The pyrazole ring is held almost right angle to the imidazole ring as indicated by the dihedral angle being 89.46°. The C–H···O intermolecular and C-

H…N intra-molecular hydrogen bond connects the molecule into a three-dimensional network. C-H…π contacts have also been observed in the molecular packing.

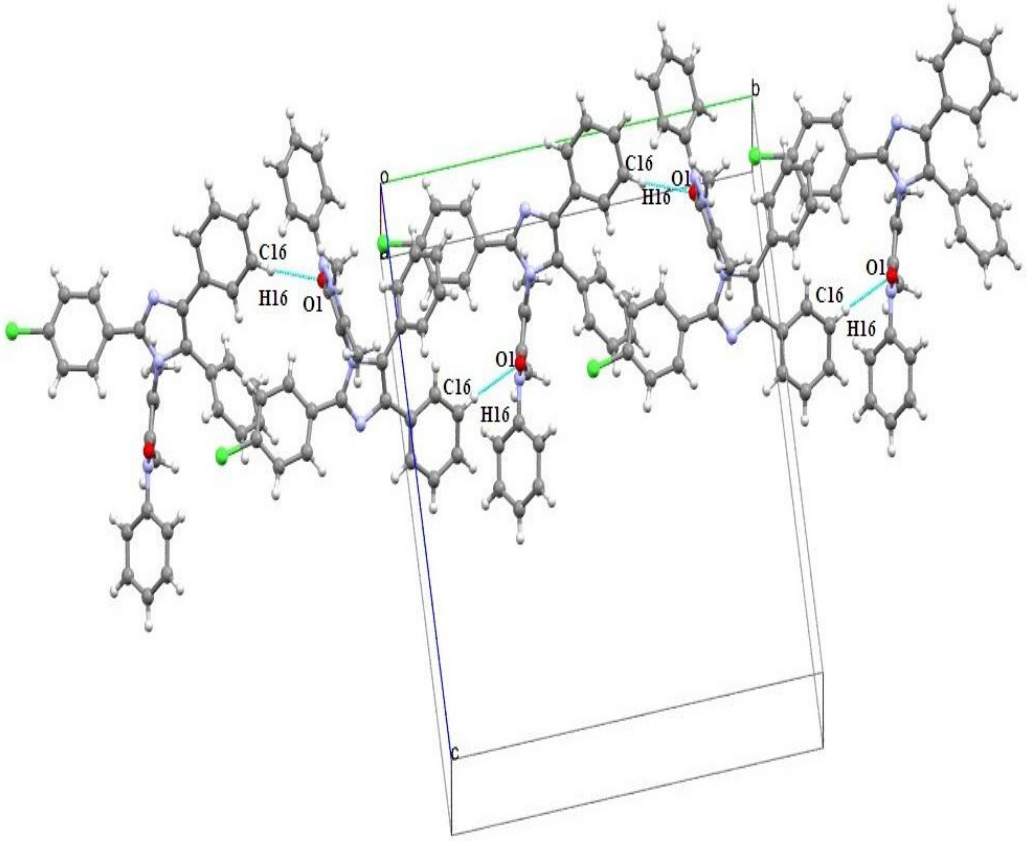

Fig.-3: Intermolecular Hydrogen Bonds Link the Molecule into Infinite Chains Along b-Axis.

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