

SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF 2-(4-(BENZYLOXY) PHENYL)-4, 5-DIPHENYL-1H-IMIDAZOLE

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ABSTRACT

The title compound 2-(4-(Benzyloxy)phenyl)-4,5-diphenyl-1H-imidazole was synthesized by a mixture of benzil (0.210 g, 1 mmol), 4-(Benzyloxy)benzaldehyde (0.212 g, 1 mmol), ammonium acetate (0.77 g, 1 mmol) and ZnO nanoparticles (0.008g, 0.1 mmol.) in 25 ml glacial acetic acid, heated at 60°C under stirring for 3 hrs. The pure product was obtained by further recrystallization from acetone, with 85% yield. It has been crystallized by using slow evaporation process in the monoclinic space group 'P 2₁/c' with unit cell parameters a = 14.2921(11) Å, b = 16.7380(12) Å, c = 9.0495(7) Å, β = 95.227(7)° and number of molecules per unit cell (Z) = 4. The crystal structure was solved by direct methods and refined by full matrix least squares procedures to a final R value of 0.0569 for 1993 observed reflections. The structure exhibits inter-molecular H-bonds of the type N-H...N and C-H...O.

Keywords: Imidazole, Crystal Structure, Direct Method, Intermolecular interaction.

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INTRODUCTION

Imidazole and its derivatives are an important class of heterocyclic compounds that exhibit a broad spectrum of biological and pharmacological activities¹. The structures of trisubstituted imidazoles are pervasive in natural products and pharmacologically active compounds, such as p38 kinase inhibitor² and cyclooxygenase-2 inhibitor³, fungicides and herbicides⁴, plant growth regulators⁵ and therapeutic agents⁶. Substituted imidazoles display biological activities like anti-inflammatory⁷, antibacterial⁸, analgesic⁹, fungicidal¹⁰ and antitumor activities¹¹.

EXPERIMENTAL

Procedure for the synthesis of 2-(4-(benzyloxy)phenyl)-4,5-diphenyl-1h-imidazole

A mixture of benzil (0.210 g, 1 mmol), 4-(Benzyloxy)benzaldehyde (0.212 g, 1 mmol), ammonium acetate (0.77 g, 1 mmol) and ZnO nanoparticles (0.008g, 0.1 mmol) in 25 ml glacial acetic acid was heated at 60 °C under stirring for 3 hrs. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and then poured into cold water with constant stirring. The solid separated was filtered by suction to afford crude product. The pure product was obtained by further recrystallization from acetone, with 85% yield. Single crystal of the purified product was developed from DMF by slow evaporation method (M.P.: 487-489 K).

X-Ray Intensity Data Collection

X-ray intensity data of the crystal (0.30 X 0.20 X 0.20 mm) having well-defined morphology were collected at 293(2)K on X'calibur CCD area-detector X-ray Diffractometer¹² equipped with MoKα

radiation ($\lambda=0.71073\text{\AA}$). The intensities were measured by employing ω scan mode for the diffraction angle ranging from 3.54 to 25.00° . A total number of 7931 reflections were measured of which 3781 were found to be unique.

The criterion ($I > 2\sigma(I)$) was employed to the unique data set and hence 1993 reflections were treated as observed. Data were corrected for Lorentz and Polarization factors. The structure was solved by direct methods using SHELXS97¹³. All non-hydrogen atoms of the molecule were located in the best E-map and Full-matrix least-squares refinement was carried out using SHELXL97¹³. The final refinement cycles converged to $R = 0.0569$ and $wR(F2) = 0.0961$ for 1993 observed reflections. The residual electron density ranges from -0.156 to $0.134\text{ e\AA}^{-3}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Table-s- 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table-1.

Table- 1: Crystal data and other experimental details

CCDC Number	1504894
Crystal description	Block
Crystal size	0.30 x 0.20 x 0.20 mm
Empirical formula	$\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_1$
Formula weight	402.48
Radiation, Wavelength	Mo $K\alpha$, 0.71073 $\text{\AA}$
Unit cell dimensions	$a = 14.2921(11)$, $b = 16.7380(12)$, $c = 9.0495(7)\text{\AA}$ $\beta = 95.227(7)^\circ$
Crystal system, Space group	Monoclinic, $P2_1/c$
Unit cell volume	$2155.8(3)\text{\AA}^3$
No. of molecules per unit cell, Z	4
Absorption coefficient	0.076mm^{-1}
F(000)	848
θ range for entire data collection	$3.54 < \theta < 25.00^\circ$
Reflections collected / unique	7931/3781
Reflections observed $I > 2\sigma(I)$	1993
Range of indices	$h = -16$ to 12 , $k = -18$ to 19 , $l = -10$ to 10
No. of parameters refined	369
Final R-factor	0.0569
$wR(F2)$	0.0961
Rint	0.0465
Rsigma	0.0943
Goodness-of-fit	0.973
$(\Delta/\sigma)_{\text{max}}$	0.001
Final residual electron density	$-0.156 < \Delta\rho < 0.134\text{ e\AA}^{-3}$

Some selected bond angles which play an important role in collating the structural properties of this molecule with the related structures are presented in Table- 2. An ORTEP¹⁴ view of the molecule with atomic labeling is shown in Figure- 2. The geometry of the molecule was calculated using the PLATON¹⁵ and PARST¹⁶ software. CCDC-1504894 contains the supplementary crystallographic data for the structure.

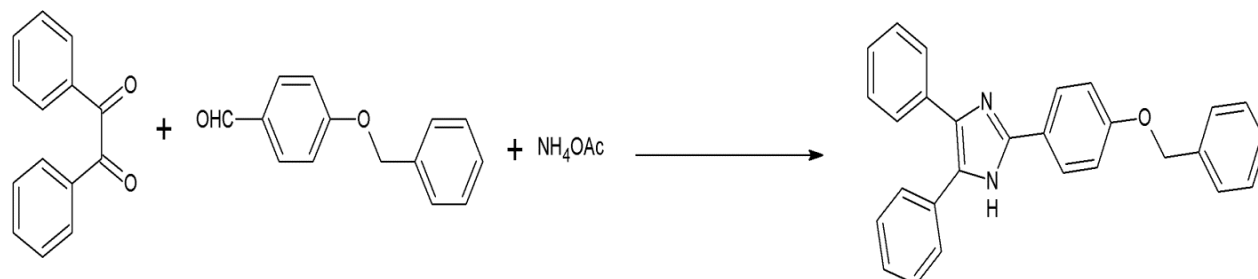


Fig.-1: Reaction Scheme.

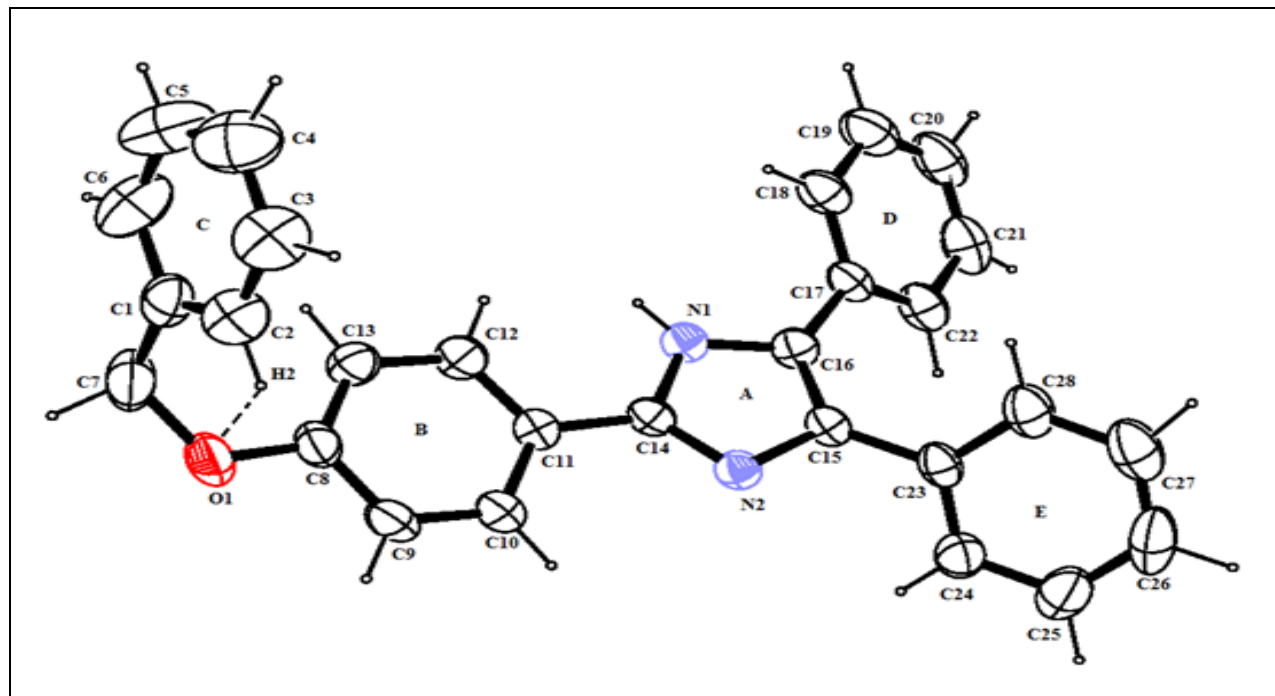


Fig.-2: Ortep view of the molecules with displacement ellipsoids at the 40% probability level.
H atoms shown as small spheres of arbitrary radii. The broken lines show the intramolecular hydrogen bonds forming S(5) motif.

Table- 2: Selected Bond Lengths and Bond angles

Bond Distances (Å)		Bond Distances (Å)	
N2-C14	1.331(2)	C1-C6	1.388(4)
N2-C15	1.387(3)	C1-C7	1.498(4)
N1-C16	1.374(3)	C8-C9	1.392(3)
N1-C14	1.369(3)	C15-C16	1.371(3)
C17-C22	1.386(3)	C15-C23	1.473(3)
C11-C12	1.385(3)	C11-C10	1.390(3)
C1-C2	1.377(4)	C8-C13	1.368(3)
C11-C14	1.457(3)	C16-C17	1.472(3)
C17-C18	1.385(3)	C23-C28	1.383(4)
Bond Angles(°)		Bond Angles(°)	

C14- N2- C15	105.99(19)	N2-C15-C23	119.9(2)
C14-N1-C16	108.2(2)	O1-C8-C9	114.8(3)
N1-C14-N2	110.2(2)	C8-O1-C7	118.2(2)
N1-C14-C11	122.6(2)	C12-C11-C14	121.0(2)
N2-C14-C11	127.0(2)	C10-C11-C14	121.2(2)
C15-C16-N1	105.6(2)	C12-C11-C14	121.0(2)
N1-C16-C17	120.4(2)	C18-C17-C16	120.3(2)
C16-C15-N2	110.0(2)	C22-C17-C16	120.5(2)
C16-C15-C23	130.0(2)	C15-C16-C17	134.0(2)
C28-C23-C15	120.9(3)	C13-C8-O1	125.5(2)

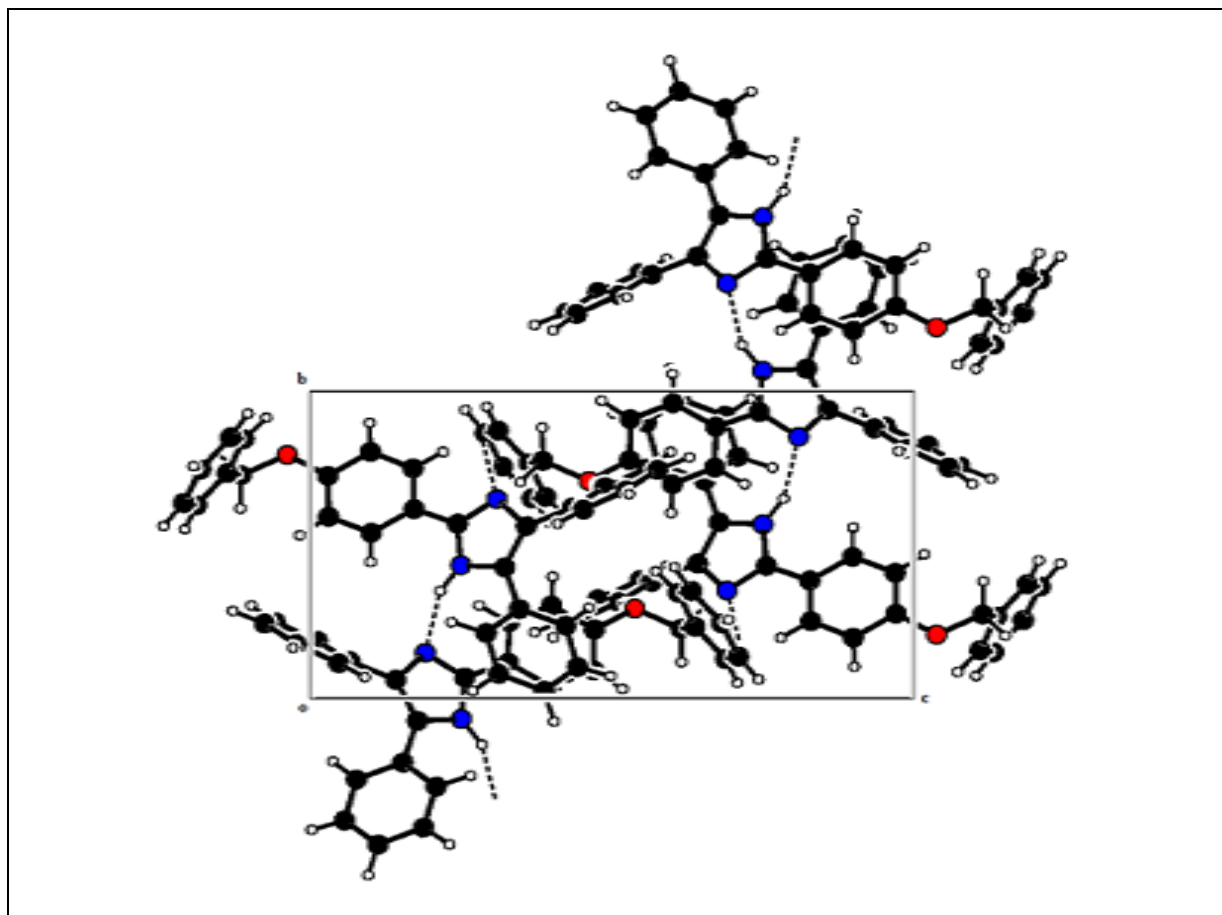


Fig.-3: Packing of the molecules viewed down the a-axis.

RESULTS AND DISCUSSION

The molecular structure containing atomic labeling is shown in Figure- 2 (ORTEP)¹⁴. X-ray diffraction studies reveal that the molecule consists of four phenyl and an imidazole ring. Phenyl ring B, D and E are attached with imidazole ring at the positions C14, C16 and C15, respectively. The structural parameters, including bond distances and angles show a normal geometry¹⁷ and are in agreement with the values observed for some related structures¹⁸⁻²⁰. The bond distances N1-C16 [1.374(3) Å], C15-C16 [1.371(3) Å], N2-C15 [1.387(3) Å], N2-C14 [1.331(2) Å] and N1-C14 [1.369(3) Å] of the imidazole ring lies within

the normal range¹⁷. Rings A, B, C, D and E are essentially planar, with atom C16, C8, C4, C17 and C26 displaced out of their mean ring planes by 0.0056(2) Å, -0.0173(3) Å, 0.0062(4) Å, 0.0052(3) Å and 0.0052(4) Å, respectively. The O1 atom attached with the carbon atom C8 is coplanar with the ring B, indicated by the torsion angles O1-C8-C9-C10 = -177.1(3)° and O1-C8-C13-C12 = 176.7(3)°, this feature can also be seen in the related structure²¹⁻²³. Three phenyl rings C, D and E are twisted from imidazole ring A with a dihedral angle of 69.22(10)°, 41.87(10)° and 50.25(10)°, respectively. Phenyl ring B attached to imidazole ring A makes a dihedral angle of 15.69(9)° and is twisted from ring C with a dihedral angle of 77.73(9)°.

Intramolecular interaction C2-H2...O1 results in a formation of five-membered ring with graph-set motif S(5) (Figure-2). In the crystal structure, adjacent molecules are interconnected through two intermolecular hydrogen bonds viz., N1-H...N2 and C28-H28...O1. The geometry of hydrogen bonding is presented in Table- 3. It is worth mentioning that, the molecular packing in the crystal structure is stabilized by two intermolecular hydrogen bonds, of which N2 and O1 work as hydrogen bond acceptors and N1 and C28 work as hydrogen bond donors, respectively. Molecular packing in the unit cell viewed down the *a*-axis is shown in Figure-3 (PLATON)¹⁵. No significant C-H... π contacts are observed in the molecular packing of title compound. The crystal structure is further stabilized by π - π interactions and detail of π - π interaction is given in Table-4.

Table- 3: Geometry of Intra and Inter molecular Hydrogen bonds

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A(°)
N1-H1...N2 ⁱ	0.96(3)	1.97(3)	2.864(3)	155.0(2)
C28-H28...O1 ⁱⁱ	0.94(3)	2.49(3)	3.424(5)	171.6(19)
C2-H2...O1	0.98(3)	2.48(3)	2.862(5)	102.9(19)

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

Table- 4: Geometry of π - π interactions*

CgI...CgJ	CgI...CgJ (Å)	CgI...P(Å)	α (°)	β (°)	Δ (Å)
Cg1...Cg2 ⁱ	3.8197(18)	3.305	10.86	20.82	1.91

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

* Cg1 and Cg2 represent the centre of gravity of imidazole and phenyl (D) rings, respectively.

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