Synthesis, characterizations, molecular structure and DFT studies of 4-benzylidene-2-(2-chloro-phenyl)-5-methyl-2,4-dihydro-pyrazol-3-one

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The title molecule 4-benzylidene-2-(2-chloro-phenyl)-5-methyl-2,4-dihydro-pyrazol-3-one, $C_{17}H_{13}N_2OCl$ (I) is synthesized and characterized by IR, NMR and X-ray single crystal diffraction analysis. Molecular geometry, vibrational wave numbers, frontier molecular orbitals and Mulliken charges of the title compound have been calculated using density functional method B3LYP at 6-311g* basis set. Title compound crystallizes in the monoclinic space group P2₁/c with a = 10.343 (3) Å, b = 11.321 (3) Å, c = 12.486 (4) Å, $\beta = 92.380$ (5)°, V = 1460.8 (7) Å³ and Z = 4. The dihedral angles between the mean plane of chloro phenyl ring, phenyl ring with the mean plane of pyrazole ring are 65.91(15)° and 21.75(17)°, respectively. After optimization by DFT method, the twisting of the central pyrazole ring with chloro phenyl ring and phenyl ring turns out to be 51.96(16)° and 1.26(14)°, respectively. The drastic differences observed in the dihedral angle calculated after treating the molecule by DFT method support our observations that molecular packing is influenced by the collective effect of weak but significant C-H...N, C-Cl... π , C-H...Cl, C-H...O and π - π interactions in the solid state which are otherwise lacking in isolated state. The optimized geometric bond lengths, bond angles and torsional angles obtained by density function theory (DFT) show good agreement with experimental data. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Pyrazole oxygen O7 and chloro phenyl carbon C13 act as bifurcated donor and acceptor in half a dozen intermolecular interactions, thereby strengthening the molecular packing.

Keywords: Pyrazole, Spectroscopy, X-ray diffraction, DFT calculations, HOMO, LUMO

1 Introduction

Pyrazole derivatives attracted much attention as they show broad spectrum of biological activities, such as antimicrobial, antipyretic, anti-inflammatory, antiviral, anticancer, insecticidal, herbicidal, plant growth regulatory and also found active against several tumour cell lines¹⁻⁷. To synthesize halogen containing heterocyclic compounds to elucidate the differences between the molecular conformations in the solid state and those in the isolated state due to the absence of weak molecular interactions⁸⁻¹⁰, here we present the synthesis, characterization, crystal structure and theoretical studies of a new chloro pyrazole derivative.

2 Experimental Details

2.1 Synthesis

Ethyl acetoacetate (i) (0.54 g) and 2-chlorophenylhydrazine (ii) (0.57 g) are mixed in 10 ml vial and

then the mixture is irradiated in a CEM discover-S class, microwave synthesizer (300 W) for 10 min. After cooling, ether (5 ml) is added and crystals are filtered. The crude product (iii) is mixed with benzaldihyde (0.5 g) in DMF (2 ml) in 10 ml microwave vial. The crude product obtained after evaporation of ethyl acetate is further purified using prep HPLC to give 24 mg of final product (iv). Reaction scheme of the title compound is shown in Fig. 1.

¹³C NMR spectra are recorded with a Fourier transform instrument at 400 MHz (Bruker). IR spectra analysis performed using Perkin Elmer Spectrum, Frequency range: 4000-400 cm⁻¹ (KBr disc).

IR (KBr, cm⁻¹): 3061 (=C-H phenyl ring), 2952 (C-H methyl), 1685(C=O), 1596 (C=N pyrazole), 1484 (C=C), 755 (C-Cl).

¹³C NMR (DMSO) δppm: 153.68 (C-3, pyrazol), 163.24 (C-4), 161.84 (C-5), 137.19 (C-9), 145.23



Fig. 1 - Reaction scheme



Fig. 2 — ORTEP view of the title molecule with atom labelling scheme and 50% probability level displacement ellipsoids

(C-8), 148.28 (C-16), 142.79 (C-18), 125.49 (C-10), 128.62 (C-13), 129.53 (C-11) 13.11 (C-6).

2.2 X-ray structure determination

Orange-red coloured square shape single crystals of the title compound, 4-benzylidene-2-(2-chloro-phenyl)-5-methyl-2,4-dihydro-pyrazol-3-one are grown from acetonitrile under controlled evaporation at room temperature. The ORTEP view of the title molecule 4-benzylidene-2-(2-chloro-phenyl)-5-methyl-2,4-dihydropyrazol-3-one drawn with 50% probability is shown in Fig. 2.

X-ray intensity data of the title compound are collected at room temperature using graphite monochromated MoK α radiation ($\lambda = 0.7107$ Å) on Bruker SMART APEX II CCD diffractometer. The

crystal structure is solved by direct methods¹¹ using the SHELXS 97 and refined by full-matrix least square techniques¹² using SHELXL 97. The final R-value is 0.0744 for 2618 observed reflections [I > 2σ (I)]. Crystallographic data and details of data collection, structure solution and refinements are listed in Table 1.

The crystallographic data of the structure described in the present paper are deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 849340, Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk. Table 1 — Crystallographic data for title compound

Chemical formula	$C_{17}H_{13}$ ClN_2O
Crystal morphology	Orange – red, square
Molecular weight	296.74
Crystal system	Monoclinic
Space group	P2 ₁ /c
Lattice parameters a	10.343(3) Å
b	11.321(3) Å
С	12.486(4) Å
β	92.380 (5)°
Number of formula units Z	4
Volume	1460.8(7) Å ³
Calculated density $D_{\rm C}$	1.349 g/cm^3
Absorption coefficient (µ)	2.61 cm^{-1}
Radiation	MoK _α
Wavelength (λ)	0.7107 Å
F(000)	616
$2\theta_{max}$	56.58°
No. of reflections measured	7133
No. of reflections used	2151 ($I > 2\sigma(I)$)
$R(\mathbf{F}^2)$	0.0765
$Rw(F^2)$	0.0982
Weighting scheme	$W=1/[\sigma^2(F_0^2) + (0.0526P)^2]$
	+ 0.5992P]where
	$P = (F_0^2 + 2F_c^2)/3$
Goodness-of-fit on F ²	1.058
No. of parameters refined	192
$(\Delta \rho)_{min}$	–0.223 eÅ ⁻³
$(\Delta \rho)_{max}$	0.218 eÅ ⁻³

2.3 Computational calculations

Geometries of the title compound are optimized at the B3LYP/6-311G* levels of theory of DFT method. In DFT methods, Becke's three parameter exact exchange-functional (B3) combined with gradientcorrected correlation functional of Lee, Yang and Parr (LYP) are used implementing 6-311G* basis set^{13,14}. Vibrational frequency calculations are computed at the B3LYP/6-311G* level of theory to predict the IR spectra of title molecule. All quantum chemical calculations are performed¹⁵ using Gaussian-09 and Gauss-View molecular visualization program¹⁶.

3 Results and Discussion

3.1 FTIR spectroscopy

Infrared spectra are recorded using KBr (4000- 400 cm^{-1}) on Perkin Elmer Spectrum GX (Fig. 3).

Few unscaled harmonic vibrational frequencies calculated by B3LYP methods using 6-311g* level are listed in Table 2 and compared with those of experimental data.

The vibrational spectral analysis have been performed based on the characteristic vibrations of the carbonyl group, methyl group, halogen group (C-Cl), amine group and phenyl group. In FTIR spectra, the bands at 1685 cm⁻¹ have been assigned to C=O stretching vibrations. The corresponding stretching



Fig. 3 — Recorded IR spectrum of the title molecule

Assignments	Experimental IR (with KBr)	Calculated (B3LYP)
C-H bond aromatic str. medium	3061	3119
CH ₃ group with pyrazole ring	2922	3003
C=O str.	1685	1669
phenyl ring C=Cstr. + C-N str.	1596	1610
phenyl ring C=C str.	1484	1489
methyl group C-H bend	1449	1444
phenyl ring C-H bend + pyrazole	1324	1332
ring C-H bend		
pyrazole ring C-H bend + C-N str.	1153	1140
pyrazole ring C-H bend	1074	1091
methyl group C-H bend	1029	1059
phenyl ring C-H bend	947	925
phenyl ring C-H twist	848	837
C-Cl str.	755	750
Skeleton deformation	648	623

Table 2 — Comparison of the observed and calculated vibrational spectra of the title compound

vibration frequency calculated using B3LYP/6-311G* methods is 1669 cm^{-1.} In the ligand, the phenyl ring carbon-carbon stretching band is observed at 1484 cm⁻¹ and the theoretically C-C phenyl band computed at 1489 cm⁻¹. The aromatic C-H stretching bands are assigned in the range 3100-3000 cm⁻¹.

3.2 X-ray structure analysis

Five-membered pyrazole ring makes the central part of the molecule with substituent chloro-phenyl ring at N1 and a phenyl ring at C4. Selected bond lengths, bond angles, torsional angles and dihedral angles are given in Table 3.

The chloro-phenyl ring twisted by $65.91(15)^{\circ}$ to the plane of pyrazole ring whereas the dihedral angle of phenyl ring with pyrazole is $21.75(17)^{\circ}$. An intramolecular interaction between O7 and C21, forms a pseudo six membered ring¹⁷ of graph-set motif S(6). The torsional angle C5-C4-C8-C16 of $4.26(3)^{\circ}$ confirms a CIS conformation of phenyl ring plane with respect to C4-C8 bond. Molecular packing diagram and the various molecular interactions such as C-H..N, C-H...Cl, C-Cl... π , C-H...O and π - π interactions are calculated using the program^{18,19} PLATON-97 and PARST (Table 4).

Pyrazole oxygen O7 of screw-related molecule [x, -y+1/2, z-1/2] forms bifurcated donor bond; both the interactions involve chloro-phenyl carbon C13 and C14 as acceptor. Chloro-phenyl carbon C13 forms bifurcated acceptor bond: the interaction involves pyrazole oxygen O7 of two screw related molecules [x, -y+1/2, z-1/2 and 2-x, 1/2+y, 1/2-z]. Pyrazole oxygen O7 of another symmetry related

Table 3 — Selected geometrical parameters of the title compound
by X-ray diffraction and theoretical calculation at the B3LYP/6-
311g* level of theoryParametersX-rayB3LYP/6-311g*Bond lengths1.730(3)1.7508
07-C5O7-C51.2165(3)1.2165NL N21.400(2)1.2022

Cl15-C10	1.730(3)	1.7508
O7-C5	1.2165(3)	1.2165
N1-N2	1.409(3)	1.3942
N1-C5	1.372(3)	1 3943
N1-C9	1.672(8) 1.417(3)	1 4146
N2-C3	1 295(3)	1 2950
C8-C4	1.255(5) 1.359(4)	1 3598
C_{0}	1.557(4) 1.456(4)	1.5570
C_{2}	1.400(4)	1.4529
C_{3}	1.499(3)	1.4944
C3-C4	1.430(4)	1.4018
(2) (1)	1.491(4)	1.4961
(C_{1}^{-}, C_{2}^{-}) ave	1.3781(5)	1.3981
(C10-C21)ave	1.3788(5)	1.3938
Bond angles		
N2-N1-C5	113.73(17)	113.0627
N2-N1-C9	119.13(17)	119.2844
C5-N1-C9	127.10(18)	126.7031
N1-N2-C3	106.07(18)	107.4809
C4-C8-C16	133.2(2)	134,4234
N2-C3-C4	112.7(2)	112,1286
N2-C3-C6	121.2(2)	120 6665
C4-C3-C6	126.0(2)	127.2049
C8-C4-C5	131.9(2)	132.2174
C8-C4-C3	124.0(2)	123.7521
C3-C4-C5	103 99(19)	104 0299
07-C5-C4	132.0(2)	131.8642
N1-C5-C4	103.46(19)	103 1208
07-C5-N1	124.5(2)	124,9952
C10-C9-C14	118.8(2)	118.7283
N1-C9-C10	121.3(2)	122.0581
N1-C9-C14	119.9(2)	119,1958
C9-C10-C11	120.7(2)	120 4371
C115-C10-C11	118 96(19)	118 3807
C115-C10-C9	120.34(17)	121 1412
C8-C16-C17	116 8(2)	116 6240
C_{17} - C_{16} - C_{21}	117.7(2)	118 2230
C8-C16-C21	117.7(2)	110.2250
Terrienel engles	125.5(2)	125.1530
l'orsional angles		
C3-C4-C8-C16	-179.9(3)	-179.9897
C5-C4-C8-C16	4.26(3)	-0.3059
C17-C16-C8-C4	-162.65(4)	-178.4428
C21-C16-C8-C4	18.69(6)	1.5854
C14-C9-N1-N2	64.04(2)	50.1916
C14-C9-N1-C5	-113.45(3)	-117.8411
Dihedral angles		
N1-N2-C3-C4-C5 and	65.91(15)	51.96 (16)
C9-C10-C11-C12-C13-C14		
N1-N2-C3-C4-C5 and	21.75(17)	1.26(14)
C16-C17-C18-C9-C20-C21		

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molecule [-X+2, -Y+1, -Z+1] interacts with C20 of the phenyl ring (Fig. 4).

Halogen contributes very actively forming C-H...hal interactions in the supra molecular aggregation. Halogen chlorine of the screw-related molecule $[x, -y+1\backslash2, z-1\backslash2]$ works as acceptor via C14-H14...Cl15. The centroid of the pyrazole ring and the phenyl ring of translated molecule [1-x, 1-y, 1-z] are at 4.437(2) Å apart in a π - π interaction. The π - π stacked molecules form a kind of distorted circular motif which is further joined by C10-Cl15... π hydrogen bond to form a molecular chain along [001] direction (Fig. 5).

3.3 Molecular geometry

A Density Functional Theory (DFT) with Gaussian-09 program package employing B3LYP (Becke three parameter Lee-Yang-Parr) method with 6-311G* basis set is used to determine optimized bond lengths and angles. Selected bond lengths, bond angles, torsional angles and dihedral angles compared with those of the experimental data and are presented in Table 3. The results indicate that most of the optimized bond lengths are slightly larger than the experimental values, attributed to the fact that the theoretical calculations are performed for an isolated molecule in gaseous phase and experimental results are of the molecules in solid state. The geometry of the solid state structure is subjected to intermolecular



Fig. 4 — View of the molecular packing on *bc* plane showing C-H...O interactions

forces, such as Van der Walls interactions and crystal packing forces. The biggest difference of bond length between the experimental and predicted values occurs at N1-C5 and Cl15-C10 bonds, 0.0223 and 0.0208Å for B3LYP method, respectively and the biggest difference of bond angle between the experimental and predicted values of 1.4109, 1.2234 and 1.2049 for N1-N2-C3, C4-C8-C16 and C4-C3-C6 bond angles, respectively at B3LYP method for 6-311G* basis set. The notable difference in the bond lengths of N1-C5 and Cl15-C10 may be attributed to the involvement of Cl15 and the oxygen O7 in number of intermolecular interactions in the solid state which is otherwise absent in the isolated state i.e. in theoretical calculations^{9,20}. The dihedral angle between the best plane of pyrazole ring N1-N2-C3-C4-C5 with those of phenyl ring plane C16-C17-C18-C19-C20-C21 and chloro phenyl ring plane C9-C10-C11-C12-C13-C14 are 1.26° and 51.96°, respectively after treating the molecule by B3LYP/6-311G* method, predicting a drastic decrease of dihedral angles by 20.49° and 13.95°. The change observed in the dihedral angles between the crystalline state and the isolated state (theoretical) supports the fact that the molecular conformation in crystalline state is influenced by collective effect of significant intermolecular interactions involving $\pi...\pi$, C-Cl... π , C-H...O, and C-H...Cl interactions. The comparatively large change in dihedral angles further supports that the constituents of phenyl ring took part in more number



Fig. 5 — View of the molecular packing showing C-H...Cl, C-hal... π and π - π interactions

of significant interactions in the crystalline state than that of the chloro phenyl ring (Table 4).

3.4 Mulliken population analysis

The Mulliken population analysis of the title molecule is calculated using B3LYP method with 6-311G* set. The bar-diagram of Mulliken charge distribution is shown in Fig. 6.

It may be noted that the oxygen atom O7 has negative charge -0.3501 by B3LYP method and the adjoining carbon atom C5 atom has the highest positive charge 0.5529. The Cl15 atom has slightly negative and bonded with negative carbon C10 atom via Van der Walls interactions. All nitrogen atoms have negative charge and the nitrogen N1 atom has more negative than nitrogen N2. Similarly all the hydrogen atoms have a net positive charge; in particular, the hydrogen atoms H13, H14, H17, H20 and H21 have significantly large net positive charge. The presence of large amount of negative charge on carbons (C13, C14, C17, C20 and C21) and the positive charge on hydrogen (H13, H14, H17, H20 and H21) atoms facilitate formation of quite a large number of intra and inter molecular hydrogen bonding interactions in the crystalline phase especially in these region, which is confirmed from the crystallographic investigations (Table. 4).

3.5 HOMO and LUMO analysis

The total energy of the title compound is -1300.4890 Hartree calculated by B3LYP/6-311G* method. There are several ways to calculate the excitation energies and the simplest one, involves the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of neutral system. Analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the

Table 4 — Intra and intermolecular interactions (distances in Å, angles in °)

A. π π interaction					
Cg(I) Cg(J)	Cg(I)Cg(J)Å	Cg(I)P Å	α	γ	
1 3 (iii)	4.437 (2)	2.813	21.75	50.65	
B. C-Cl π interactions					
Y-X(I)Cg(J)		X(I)Cg Å	Y-XCg °	γ	
C10-Cl15Cg (1) (iv)		3.903 (19)	164.04(10)	27.82	
C. Intermolecular Hydrogen bonding	interactions				
D-HA	d (D-H) Å	d (D-A) Å	d (H-A) Å	(D-HA)°	
C21-H21O7 (i)	0.93(3)	3.024(4)	2.278(2)	137.14(16)	
C8-H8N2 (vii)	0.93(4)	3.722(4)	2.937(2)	142.95(15)	
C13-H13O7 (iv)	0.93(3)	3.538(4)	2.974(2)	120.44(19)	
C14-H14O7 (iv)	0.93(3)	3.505(4)	2.911(2)	123.00(17)	
C13-H13O7 (v)	0.93(3)	3.437(4)	2.687(2)	138.33(18)	
C20-H20O7 (vi)	0.93(3)	3.430(4)	2.620(2)	145.86(19)	
C17-H17Cl15 (iii)	0.93(3)	3.784(4)	2.980(1)	145.66(17)	
C14-H14Cl15 (iv)	0.93(3)	3.778(3)	2.885(1)	161.43(16)	
Symmetry Code : (i) [x,y,z]; (ii)	[-x+1,y+1/2,-z-1/2]; (i	ii) [-x+1,-y+1,-z+1]; (iv	<i>v</i>) $[x,1/2-y,-1/2+z];$ (v)	[-x+2,+y-1/2,-z+1/2];	
(vi) [-x+2, -y+1, -z+1]; (vii) [-x+1, +y+1, -z+1/2]					



Fig. 6 — Mulliken charge distributions chart of the title compound using B3LYP and PBE1PBE methods with 6-311G* level



Fig. 7 — Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)

first exited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Fig. 7 shows the HOMO and LUMO orbitals of the title compound obtained by B3LYP/6-311G* method.

The energy gap of HOMO – LUMO is -0.22385 a.u. by B3LYP/6-311G* method, it explains the eventual charge transfer interaction within the molecule. The dipole moment calculated by B3LYP/6-311G* method is 3.1892.

4 Conclusions

Title compound 4-benzylidene-2-(2-chlorophenyl)-5-methyl-2,4-dihydro-pyrazol-3-one has been synthesized and its crystal structure has been determined. The optimized DFT data, bond lengths, bond angles, torsional angles and dihedral angles, reveal a better agreement between the experimental and computed one. Theoretical data conforms that the presence of intermolecular interactions in crystalline significantly influences the molecular state conformations. In the absence of potential donoracceptor group in the title compound, diversified interactions viz C-H...O, C-H...N, C-H...Cl, C-Cl... π and π - π are responsible for the stability of the supramolecular structure. The interactions involving Cl are though weak but being directional facilitate in orienting the molecules to generate supramolecular motifs of specific properties.

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