Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2014, 5(6):18-22

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Structural and conformational studies of (E)-methyl 2-(3-isopropyl-1-methyl-2,6-diphenylpiperidin-4-ylidene)hydrazinecarboxylate

T. Mohandas[a*], C. Udhaya Kumar[b], V. Kathiravan[c], B. Arul Prakasam[d], P. Sakthivel[e] and T. Vidhyasagar[f]

[a]*Department of Physics, Shri Angalamman College of Engineering and Technology, Tiruchirappalli, India*
[b]*Department of Chemistry, Annamalai University, Chidambaram, India*
[c]*Department of Physics, Government Arts College, Karur, India*
[d]*Department of Chemistry, Annamalai University, Chidambaram, India*
[e]*Department of physics, Urumu Dhanalakshmi College, Tiruchirappalli, India*
[f]*Department of Chemistry, Annamalai University, Chidambaram, India*

ABSTRACT

In the title compound $C_{23}H_{30}N_3O_2$ the piperidine ring exists in a chair conformation. The phenyl rings attached to the centre piperidine ring at 2 and 6 positions. These two phenyl rings make a dihedral angle of 54.81(19)\% with respect to the piperidine ring. The phenyl rings and the methyl group substituted on the hetrocyclic system has an equatorial orientation. Further in this structure the molecules are linked with N---H...O and C---H...O interactions.

Key words: Piperidone, hydrogen bonding.

INTRODUCTION

Bioactive heterocyclic ring systems are used in the past and recent years due to their wide variety of biological properties (1). such as antitumor (2), anti-inflammatory (3),central nervous system (4), anticancer (5), and antimicrobial activity (6).Piperidone is a promising candidate for the synthesis of various heterocycles and biologically active compounds. 2,6-diaryl piperidones are interesting intermediates in most of the synthesis, because of the known therapeutic properties of piperidones due to the presence of a keto function that facilitates the introduction of other new substituent's on the piperidine ring, there are widely used in the synthesis of new molecules.

MATERIALS AND METHODS

3-isopropyl-1-methyl-2,6-diphenylpiperidin-4-one (1 mmol) and a few drops of glacial acetic acid were stirred in absolute ethanol for 15min in ice cold condition. Then, methyl carbazate (1mmol) was added and stirred for an additional 45 min. After completion of the reaction, addition of water (50 mL), resulted the precipitate which was collected by filtration and washed with a large portion of cold water. The crude product thus collected was recrystallized from ethanol.

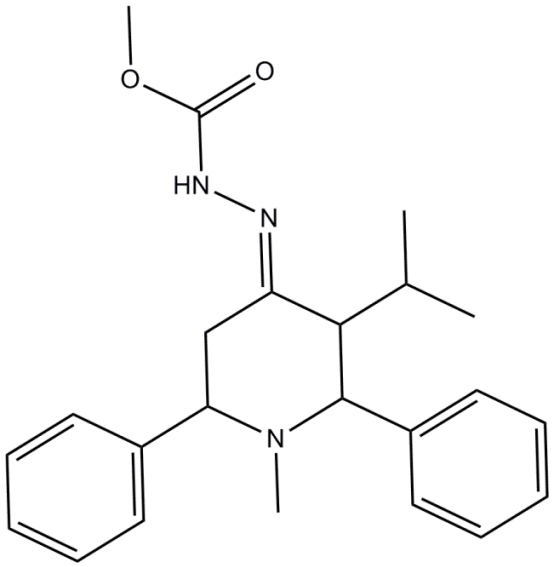

Figure 1 Figure 1. shows the molecular structure of the title compound

Intensity Data Collection

X-ray data were collected on a Bruker AXS (Kappa APEX2)[7] CCD area detector using ω and ψ scan mode. A small crystal of size 0.20 × 0.17 × 0.16 mm was chosen and its quality was checked using polarizing microscope. Cell refinement and data reduction were carried out by using APEX2/SAINT-NT [7]. Sets of two standard reflections were monitored for every one hour of exposure during the data collection and there was no noticeable change in the intensity observed. A total of 14385 reflections were collected resulting in 2966 independent reflections of which 2191 had I > 2σ (I), were considered as observed reflections. The intensities were corrected for Lorentz and polarization effects. Absorption corrections were made with **SADABS**[7].

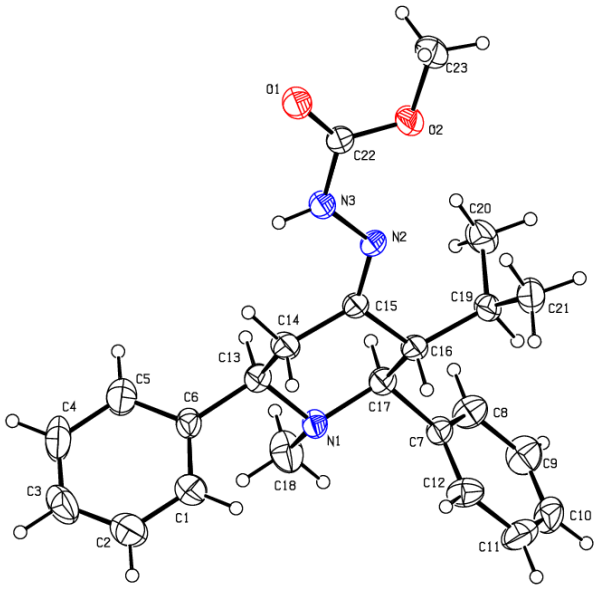

Figure 2.shows the ortep diagram of the title molecule

Structure Solution and Refinement

The refinement was carried out by SHELXL-97[8]. The positions of the hydrogen atoms bound to the O and C atoms are identified from the difference electron density maps and their distances are geometrically optimized. The H atoms associated with the hydroxyl groups are constrained to a distance of d(O---H) = 0.82\%A; and Uiso(H) = 1.5Ueq(O). The hydrogen atoms bound to the C atoms are treated as riding atoms, with d(C---H)=0.93 and Uiso(H) = 1.2Ueq(C) for aromatic, d(C---H)=0.97 and Uiso(H)=1.2Ueq(C) for methylene and d(C---H)=0.96 and Uiso(H) =1.5Ueq(C) for methyl groups.

The weighting scheme [9] adopted during the final cycle of refinement is

w=1/[\s^2^(Fo^2^)+(0.0635P)^2^+0.8252P]

where P=(Fo^2^+2Fc^2^)/3.The geometric calculations were performed using the PARST[10,11] and PLATON [12].

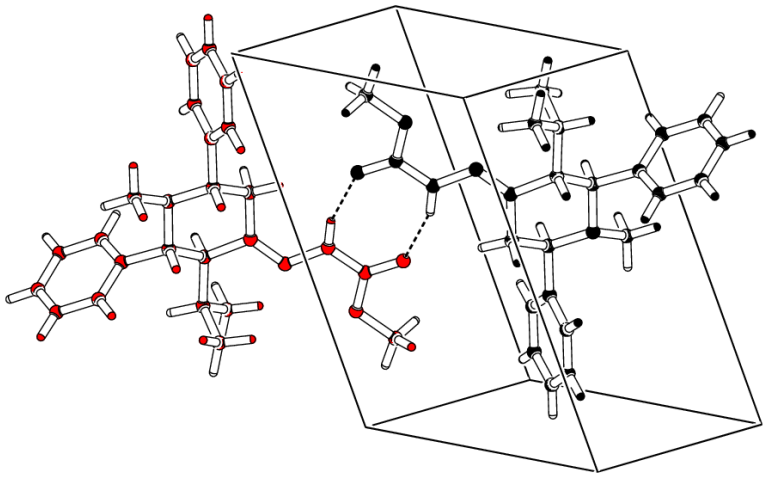

Figure 3.shows the packing diagram of the title compound

RESULTS AND DISCUSSION

The piperidine ring (N1/C13/C14/C15/C16/C17) adopts the chair conformation with the puckering parameters Q=0.5333\%A, \q=6.71\% and \f=4.641\%. (13). The torsional angles of (C15/C14/C13/C6) and (C19/C16/C17/C7) are 175.88\% and 54.62\% respectively. The bond distances and bond angles in the title compound agree very well with the corresponding values(14) reported in closely related compound(15). The piperidine ring makes the dihedral angle of 80.96\% and 89.63\% with the phenyl rings at the 2 and 6 positions respectively. In each layer of hydrazinecarboxylate, the hydrogen bonds generate a graph set motif R~2~^2^(10),(16,17). The dihedral angle between the two phenyl rings is54.80\%.

Table 1. Crystal data and structure refinement of the title compound

Cell:	a= 8.3535(6)	b=11.6814(7)	c= 12.2834(9)
	α= 97.404(4)	$_{\beta}$ =102.337(4)	$_{\gamma}$= 110.829(4)
Wavelength	: 0.71073		
Temperature	: 293K		
Volume (Å3)	: 1066.52(13)		
Density (g cm^{-1})	: 1.18		
Crystal system	: Triclinic		
Space group	: -P 1		
Hall group	: P -1		
Moiety formula	: $C_{23}H_{30}N_3O_2$		
Formula weight	: 379.49		
Abs.coefficient(mm^{-1})	: 0.076		
F(ooo)	: 407.9		
No.of reflections	: 2966		
No.of parameters	: 254		
Goof	: 1.075		
Shift/esd max	: 0.008		
Shift/esd mean	: 0.002		
Delta-rho(e Å-3)max	: 0.432		
Delta-rho(e Å-3)min	: -0.190		
RI : 0.081	WR2 all : 0.163		
RI observed: 0.057	WR2 observed : 0.143		
R merge	: 0.028		
AvI/sig(I)	: 42.02		
h,k,l min : -9,-12,-13	h,k,l max : 9,12,13		
Refinement method	: Full-matrix least-square on F^2		
Data completeness=0.964	Theta(max)= 23.29		

Table 2: Torsional angles of non –hydrogen atoms

ATOMS	ANGLES
C6 C13 C14 C15	175.9(2)
C18 N1 C13 C14	-178.0(3)
C17 N1 C13 C14	-58.3(3)
C18 N1 C13 C6	60.3(3)
C17 N1 C13 C6	179.9(2)
C1 C6 C13 N1	50.2(4)
C5 C6 C13 N1	-130.6(3)
C1 C6 C13 C14	-72.3
C5 C6 C13 C14	106.9(3)
C15 C16 C19 C20	-59.2(3)
C13 N1 C17 C16	58.2(3)
C12 C7 C17 N1	59.7(3)
C8 C7 C17 N1	123.2(3)
C12 C7 C17 C16	63.5(3)
C8 C7 C17 C16	-113.5
C19 C16 C17 C7	54.6(3)
C17 C16 C19 C20	69.6(3)
C15 C16 C19 C21	69.4(3)
C17 C16 C19 C21	-161.9(2)

Table3: Hydrogen bonding geometry (Å, º) (D-donor; A-acceptor; H-hydrogen) for compound

D	H	A	D-H	H..A	D..A	D-H..A	A-SITE
N3	H3'	O1	0.8600	2.0500	2.864(3)	158.00	2_766
C14	H14A	N3	0.9700	2.4800	2.854(4)	103.00	
C14	H14A	O1	0.9700	2.4500	3.411(4)	173.00	2_766
C20	H20B	N2	0.9600	2.4400	3.012(4)	118.00	
C21	H21A	N2	0.9600	2.4600	3.023(5)	117.00	

 # symmetry code:(i) 2-x,1-y,1-z

CONCLUSION

The title compound exhibits the triclinic crystal system with the space group P -1.This crystal structure packing was stabilized by intra molecular N-H...O, C-H...O and C-H...N interactions. Further, the cg-cg interaction also found

in this structure with the symmetry code:-x,1-y,-z and -1+x,-1+y,z. Because of poor quality of the crystal specimen, a small proportion of reflection is observed.

Acknowledgement
The authors thank Dr. W. Christraj, Principal, Shri Angalamman college of engineering and technology, Tiruchirappalli, India for his support throughout this work.

REFERENCES

[1] Weintraub, P. M., Sabol, J. S., Kane, J. M. & Borcherding, D. R. *Tetrahedron*,(**2003**) ,59, 2953--2989.
[2]Arutyunyan, G. L., Chachoyan, A. A., Shkulev, V. A., Adamyan, G. G.,Agadzhanyan, T. E. & Garibdzhanyan, B. T. *Khim Farm.zh*,(**1995**) ,29, 3335.
[3]Jobin, C., Bradham, C. A., Russo, M. P., Juma, B., Narula, A. S., Brenner, D.A. & Sartor, R. B. *J. immunol*,(**1999**),163, 3474--3483.
[4] Ganellin, C. R. & Spickett, R. G. *J. Med. Chem.* (**1965**), 8, 619--625.
[5] Ileana, B., Dobre, V. & Niculescu-Duvaz, I., J. *Prakt. Chem*. (**1985**).,327, 667--674.
[6]Kumar, S., Narain, U., Tripathi, S. & Misra, K.,*Bioconjugate Chem*. (**2001**),12, 464--469.
[7] Bruker,APEX2,SAINT,and SADABS. BrukerAXIS Inc.,Madison,Wisconsin,USA.2008
[8] Sheldrick, G. M. *Acta Cryst.A*, **2008**, 64, 112--122.
[9] Wilson, A. J, *Acta Cryst*, **1976**, A32, 994.
[10] Nardelli, M.. *Comput. Chem.* **1983b,** 7, 95-98
[11] Nardelli, M. *J. Appl. Cryst*.**1995**, 28, 659.
[12] Spek, A. L. *Acta Cryst* D,**2009**,65, 148--155.
[13] Cremer, D. & Pople, J. A.. *J. Am. Chem. Soc*, **1975**,97,1354--1358.
[14] Allen, F. H. *Acta Cryst. B.*,(**2002**),58, 380--388.
[15a] Park, D., Ramkumar, V. & Parthiban, P., *Acta Cryst.E*, (**2012a**),68, 0524.
[15b] Park, D., Ramkumar, V. & Parthiban, P. *Acta Cryst.E*, (**2012b**),68, 0525.
[16] Etter, M. C., *Acc.Chem.Res.*, (**1990**),23,120-126.
[17] Bernstein, J., Etter, M. C. & Leiserowitz, L. *Structure Correlation*,Vol.2 edited by H.B.Burgi & J.D. Dunitz, (**1994**), pp.431-507.New York: VCH.