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Structural and conformational studies of 1,3,3-trimethyl-2,6-diphenylpiperidin-4-one

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ABSTRACT

In this title compound $C_{20}H_{23}NO$, the piperidine ring adopts chair conformation. The asymmetric unit consists of two molecules. The phenyl rings and the methyl group are substituted in the equatorial orientations of the heterocyclic ring. The dihedral angle between the two phenyl rings of both the molecules are 57.10(17) ° and 56.88(17)°respectively. Further the chain reaction which propagates along b axis with C-H...pi interactions stabilizes the structure . Heterocycles form a core of drug molecules with specific biological activities. QSAR studies are done continuously to improve the desired properties because stereo chemical orientations of groups present in organic molecules make the molecule active or inactive towards microbes, cell lines etc. So structural elucidation of organic molecules becomes an important area in organic synthesis. In this context we report the structure of the title compound.

Key words: Crystal structure, Piperidone, puckering, hydrogen bonding

INTRODUCTION

Piperidine class of compounds and its derivatives have been found to exhibit remarkable antibacterial and antitumor properties[1,2].Piperidin-4ones, belonging to the category of heterocycles containing nitrogen were studied widely due to their various biological properties such as antiviral, bactericidal, anti-tumor, anti-histaminic etc. The blocking of second position from the ketone function in the piperidones by alkyl groups was reported to increase their biological potency [3]. Further piperidine based chemical motifs with aryl substituent's at second and sixth positions of the ring make them potent microbial agents [4].Introduction of a methyl group at the ring nitrogen of the 4-piperidones is said to increase the cytotoxicity towards HeLa cells [5].Due to the above reason ,the title compound is undergone to X-ray diffraction method to study the structure of the compound. The molecular structure of the title compound is shown in fig.1

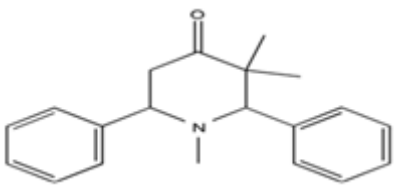

Figure 1

MATERIALS AND METHODS

A mixture of 3-methylbutan-2-one(5.4 mL, 0.05 mol), benzaldehyde (10.3 mL, 0.1 mol) and ammonium acetate(3.9g, 0.05 mol) were dissolved in ethanol(5o mL) and heated to boiling. The solution becomes orange yellow in colour after cooled to room temperature and 50 ml of diethyl ether was added followed by concentrated HCl in drop wise manner to precipitate 3, 3-dimethyl-2, 6-diphenylpiperidin-4-one hydrochloride salt. Next the hydrochloride salt was separated from solution by filtration and made into a paste with acetone and neutralized with aqueous ammonia solution, diluted with water to get the free base(8.4g, 60%). The crude product obtained is recrystallized from ethanol to get it in pure state. Piperidin-4-one thus obtained was methylated at the first position by refluxing the same(1.47 g, 5mmol) in acetone(20 mL)using iodomethane(0.31 mL, 1 eq.) and the base potassium carbonate(0.7g, 1 eq.) yield:1.25g (85%).The compound was dissolved in ethanol and allowed to slow evaporation.

Intensity Data Collection

X-ray data were collected on a Bruker AXS (Kappa APEX2)[6] CCD area detector using ω and ψ scan mode. A small crystal of size 0..22 × 0.18 × 0.17 mm was chosen and its quality was checked using polarizing microscope. Cell refinement and data reduction were carried out by using APEX2/SAINT-NT [6]. 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 17098 reflections were collected resulting in 6440 independent reflections of which 2718 had I > 2σ (I), were considered as observed reflections. The intensities were corrected for Lorentz and polarization effects. Absorption corrections were made with **SADABS**[6].

Structure Solution and Refinement

The refinement was carried out by SHELXL-97[7].Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2> 2sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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. All the hydrogen atoms were geometrically fixed and allowed to ride on their parent atoms with C-H= 0.93 - 1.01(3) Å,and Uiso(H) = 1.3Ueq(C).

The ortep diagram is shown in fig 2.

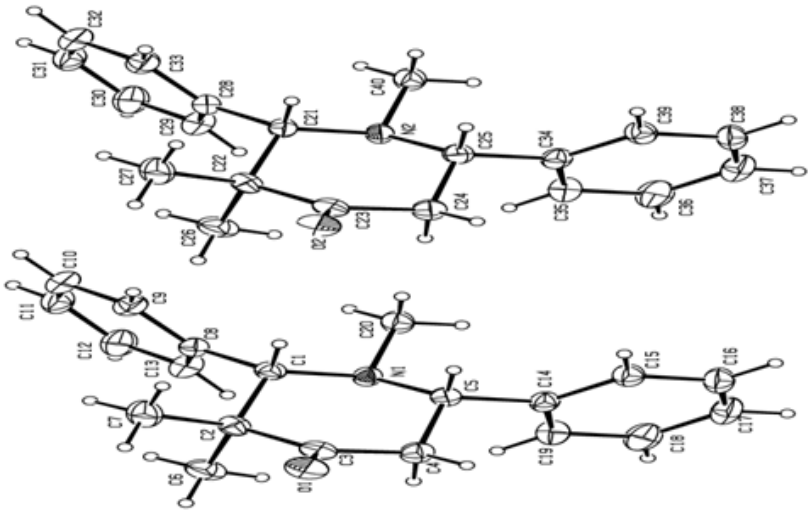

Figure 2

The weighting scheme [8] adopted during the final cycle of refinement is
w=1/[\s^2^(Fo^2^)+(0.0808P)^2^+0.2210P] where P=(Fo^2^+2Fc^2^)/3'

The geometric calculations were performed using the PARST[9,10] and PLATON [11]. The packing diagram of the title compound is shown in fig.3.

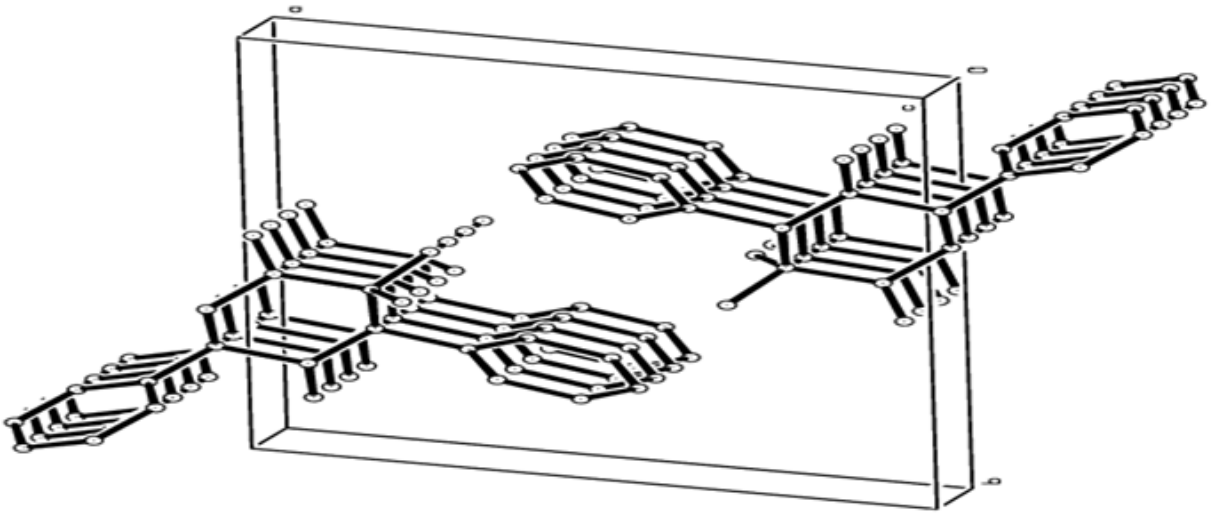

Figure 3

RESULTS AND DISCUSSION

The phenyl rings are perfectly planar and makes the dihedral angle of 57.10(17)° and 56.88(17) ° respectively. The torsional angle of C5/C14-C16 and C8/C1/N1/C5 are 179.4(3) ° and 177.4(3) ° respectively.
The sum of bond angles around atoms N1 is 328.6(6) ° and N2 is 329.0(6) °indicate sp^3 hybridization. Among the tricyclic system the piperidine ring adopts chair conformation with the puckering parameters of piperidine in both molecules (N1\C1-C5) and (N2\C21-C25) are Q=0.533(3) Å, Theta 7.0(3)° , phi is 332(3)° and Q=0.537(3) Å, Theta 174.3(3)° , phi is 211(4)° respectively.[12].The bond length and bond angles are very well agree with the standard values.[13]

The chain reaction propagates along b axis. Further the structure is stabilized by C-H...pi interactions.

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

Cell:	a=10.9758(44)	b=12.5269(51)	c= 12.9246(52)
	α=91.168(6)	β = 108.005(6)	γ= 99.186(5)
Wavelength			0.71073
Temperature			293K
Volume (Å3)			1663.73(41)
Density (g cm-1)			1.17
Crystal system			Triclinic
Space group			P-1
Hall group			-P 1
Moiety formula			C20 H23 N1 O1
Formula weight			293.4
Abs.coefficient(mm^{-1})			0.071
F(ooo)			631.9
No.of reflections measured			17098
No.of Uniq. reflections			6400
No.of reflections observed			2718
No.of parameters			428
Goof			0.971
Shift/esd max			2.464
Shift/esd mean			0.369
Delta-rho(e Å-3)max			0.179
Delta-rho(e Å-3)min			- 0.171
RI :	0.081	WR2 all	0.171
RI observed: 0.046		WR2 observed	0.138
R merge			0.023
AvI/sig(I)			40.32
h,k,l - max : 13,15,15	h,k,l – min		-13,-15,-15
Refinement method			Full-matrix least-square on F^2
Data completeness= 0.978			Theta(max)= 26.1 Theta(min)=1.7

Table 2: Torsional angles of non –hydrogen atoms

Atoms				Angle
C5	N1	C1	C2	-57.0(3)
C20	N1	C1	C2	-176.4(3)
C5	N1	C1		177.4(2)
C20	N1	C1	C8	58.0(3)
C1	N1	C5	C14	-179.5(2)
C20	N1	C5	C14	-59.9(3)
C1	N1	C5	C4	58.7(3)
C20	N1	C5	C4	178.3(2)
C25	N2	C21	C28	177.4(2)
C40	N2	C25	C34	-59.4(3)
C21	N2	C25	C34	-179.5(2)
N2	C21	C28		57.9(3)
C40	N2	C25	C24	178.4(3)
C8	C9	C10		-0.7(5)
C1	C8	C13	C12	-177.5(3)
C5	C14	C15	C16	179.4(3)
C5	C14	C19	C18	-179.9(3)

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
C11	H11	cg6	0.93	2.85	3.62	141	1_655
C31	H31	cg3	0.93	2.86	3.623	140	1_656

Symmetry code: (i) 1+X,Y,Z (ii) 1+X,Y,1+Z
Cg3 is the centroid of C8-C13atoms and cg6 is the centroid of C28-C33atoms.

CONCLUSION

The title compound adopts triclinic cell system with space group p-1**.** The centre piperidine ring adopts a chair conformation with the standard values of puckering parameter. As the center piperidine shows mild chirality, it may result in minor translation. It may be the cause for generating Pseudo space group P-1.Chiral molecules are incompatible with an inversion centre or (glide) planes.

Heterocyles form a core of drug molecules with specific biological activities. QSAR studies are done continuously to improve the desired properties because stereo chemical orientations of groups present in organic molecules make the molecule active or inactive towards microbes, cell lines etc. So structural elucidation of organic molecules becomes an important area in organic synthesis. In this context we report the structure of the title compound .

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