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Crystal structure of 7-chloro-2,3,3a,4,9,9a-hexahydro-3,9,9-trimethyl-5-nitro-1H-cyclopenta[*b*]quinoline

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Abstract : The title compound C_{16} H_{19} Cl N_2 O_2 is the product of reaction between 4-chloroaniline and melonal in the presence of cupric nitrate and HCl. The product is the resultant of nitration of the aromatic ring and electrophilic aromatic cyclization. The heterocyclic ring at the center adopts a half-chair conformation and the five-membered ring has an envelope conformation. The crystal structure is stabilized by intra-molecular hydrogen bond. The molecular structure is stabilized by an intra-molecular N—H···O hydrogen bond, with an S(6) ring motif.
Key words: crystal structure, quinolone, N—H···O hydrogen bond.

Introduction

Tacrine is used to treat the symptoms of mild to moderate Alzheimer's disease and approved by United States Food and Drug Administration in 1993[1]. One of the earliest and biggest changes the brain of Alzheimer's disease is that there is less of a chemical messenger called acetylcholine (ACh). Tacrine slows the breakdown of ACh, so it can build up and have a greater effect. It was the first centrally acting cholinesterase inhibitor approved for the treatment of Alzheimer's disease. The title compound is a congener of tacrine, has also been reported to be effective anti-alzheimeric agents[2,3].

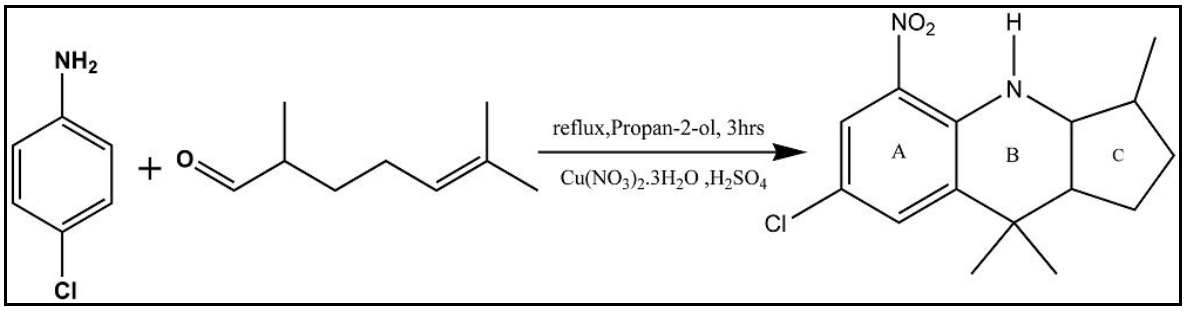
Experimental

Crystals suitable for xray-diffraction studies were obtained by slow evaporation method. Data collection was carried-out using Oxford Diffraction Xcalibur Sapphire3 with graphite mono-chromatized Mo-Kα radiation (λ=0.71703 Å). The structure was solved by direct methods and refined on F^2 by full-matrix least squares procedures using the SHELXL programs[3]. The hydrogen atoms were identified using difference fourier. was used to create the image. For molecular graphics ORTEP-3[4] program and Mercury[5] were used. The crystallographic data of the molecule is listed in Table-1.

Table:1 Crystallographic data of the title compound

Empirical formula	C15 H19 Cl N2 O2
Formula weight	294.77
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	P-1
Unit cell dimensions	a = 8.9847(13) Å α = 111.493(4)^0
	b = 9.1971(7) Å β = 100.432(5) ^{0}
	c = 9.8207(7) Å γ = 97.188(5) ^{0}
Volume	726.17(13) Å^3
Z, Calculated density	2, 1.348 Mg/m^3
Absorption coefficient	0.266 mm^{-1}
F(000)	312
Crystal size	0.19 x 0.15 x 0.11 mm
Theta range for data collection	2.30 to 26.33^0
Limiting indices	-11<=h<=11, -11<=k<=10, -10<=l<=12
Reflections collected / unique	9988 / 2903 [R(int) = 0.0229]
Completeness to theta = 26.33	98.2 %
Max. and min. transmission	0.9713 and 0.9512
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2903 / 0 / 249
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0978
R indices (all data)	R1 = 0.0512, wR2 = 0.1102
Largest diff. peak and hole	0.244 and -0.191 e.Å^{-3}

Synthesis of the compound



The quinoline derivative was prepared by the condensation 2,6-dimethyl-5- heptenaldehyde and 4-chloro aniline in 1:1 molar ratio by refluxing in propan-2-ol and nitration of the resulting compound using $Cu(NO_3)_2$.$3H_2O$ using H_2SO_4 as a catalyst. The mixture was left under reflux for 3 h. The solution was then left at room temperature. The solid product formed was separated by filtration, purified by crystallization

with ethanol washed with acetone and then dried in a vacuum over anhydrous calcium chloride (Vimal.*et al.*, 2014). The brown colored product was formed in 86% yield.

Results and Discussion

The title molecule has three fused rings consisting of two six- and one five-membered rings (A/B/C). The A/B ring junction is *trans*-fused and B/C is *cis*-fused. The central ring B adopts a twist chair conformation with the puckering parameters q2= 0.441(1) and φ2= 193.9(3) . The C8/C14/C23/C13/C ring has an envelope conformation, with C8 displaced from the other atoms (r.m.s. deviation = 0.026 Å) by 0.683 (6) Å. The puckering are parameters. q2= 0.422(1) and φ2= 174.7(3) . The packing is stabilized by weak intra-molecular N-H…O, C-H…O interactions. The N1—O2···H2A bond closes an S(5) ring motif. Table 1 & 2 gives the hydrogen bonding geometry and selected bond lengths , bond angles respectively Figures 1 & 2 give the ORTEP diagram and the packing of the molecules in the crystal cell respectively.

Table 1: Hydrogen bond geometry

N_ H…O	D-H(Å)	H…A(Å)	D---A(Å)	D-H…A(°)
N_H2A…O2	0.86	1.97	2.617(2)	132

Table 2: Selected Bond lengths (Å) Selected bond angles (°)

Cl(1)-C(1)	1.7435(17)	O(1)-N(1)-O(2)	121.73(14)
N(1)-O(1)	1.2239(18)	O(1)-N(1)-C(3)	118.05(15)
N(1)-O(2)	1.2294(18)	O(2)-N(1)-C(3)	120.22(13)
N(1)-C(3)	1.448(2)	C(1)-C(2)-C(3)	118.79(14)
C(2)-C(1)	1.355(2)	C(22)-N(2)-C(8)	121.18(14)
C(2)-C(3)	1.394(2)	C(2)-C(3)-C(22)	122.68(14)
N(2)-C(22)	1.352(2)	C(2)-C(3)-N(1)	115.51(13)
N(2)-C(8)	1.442(2)	C(22)-C(3)-N(1)	121.80(14)
C(3)-C(22)	1.417(2)	C(5)-C(6)-C(1)	122.05(15)
C(6)-C(5)	1.372(2)	C(6)-C(5)-C(22)	119.20(13)
C(6)-C(1)	1.393(2)	C(6)-C(5)-C(10)	119.72(14)
C(5)-C(22)	1.435(2)	C(22)-C(5)-C(10)	121.08(14)
C(5)-C(10)	1.543(2)	C(2)-C(1)-C(6)	120.69(15)
C(10)-C(9)	1.532(2)	C(2)-C(1)-Cl(1)	119.65(13)
C(10)-C(12)	1.536(2)	C(6)-C(1)-Cl(1)	119.65(13)
C(10)-C(11)	1.537(2)	C(9)-C(10)-C(12)	108.76(15)
C(8)-C(9)	1.508(2)	C(9)-C(10)-C(11)	113.01(15)
C(8)-C(14)	1.523(2)	C(12)-C(10)-C(11)	108.59(16)
C(14)-C(15)	1.508(3)	C(9)-C(10)-C(5)	106.74(12)
C(14)-C(23)	1.538(3)	C(12)-C(10)-C(5)	110.35(14)

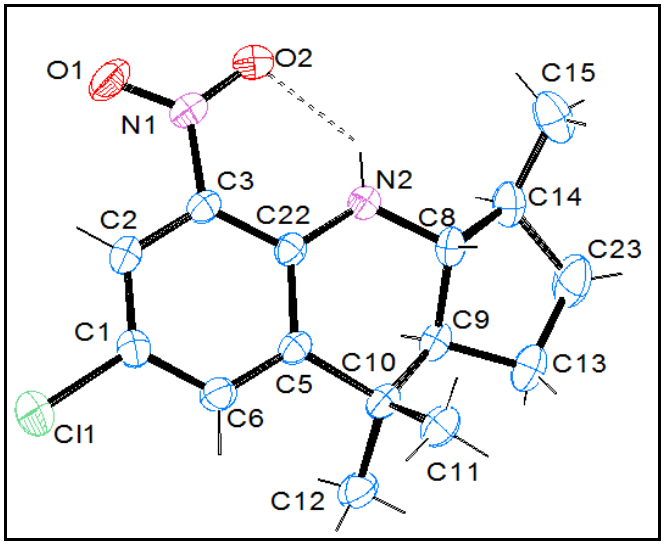


Fig 1: ORTEP diagram of the molecule drawn at 30% probablility along with S(6) motif

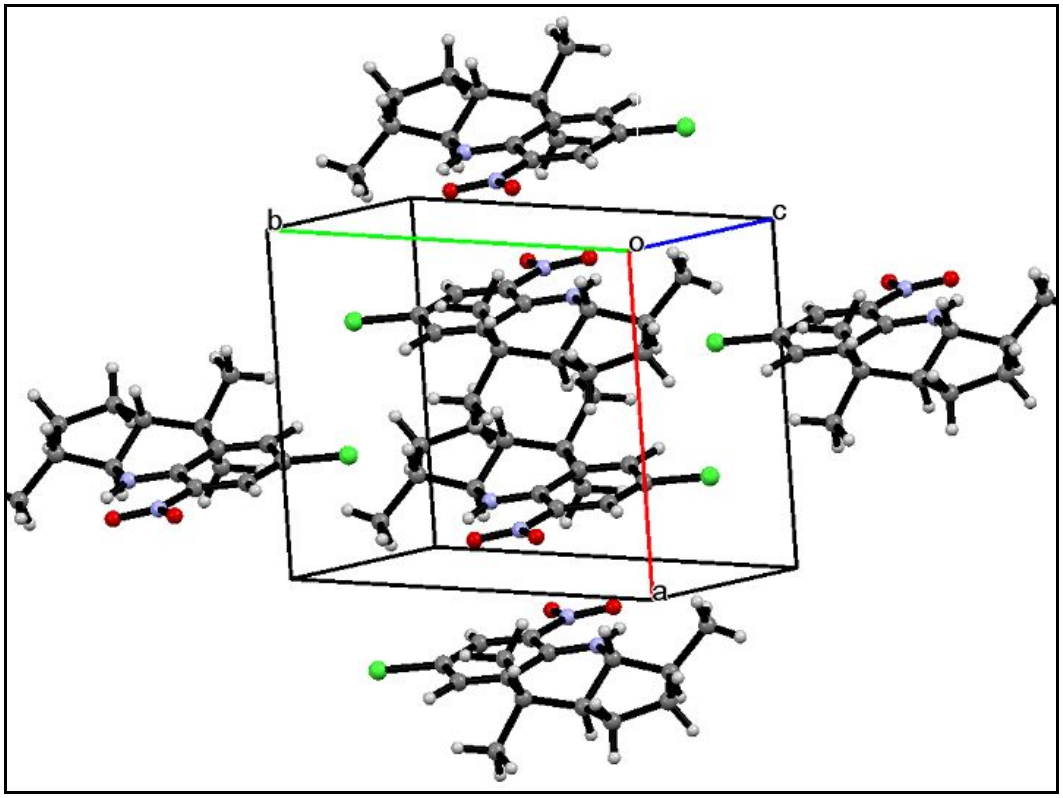


Fig 2. Crystal Packing viewed down ab-plane

Results

The crystal structure of a novel quinoline was studied using single crystal X-ray diffraction method is reported The crystal structure is stabilized by C---H…O and Vander waals interactions.

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