

Crystal Structure of 3-Chloromethyl-(3-phenyl-oxiranyl)phenyl Methanone: New Monoclinic Polymorph

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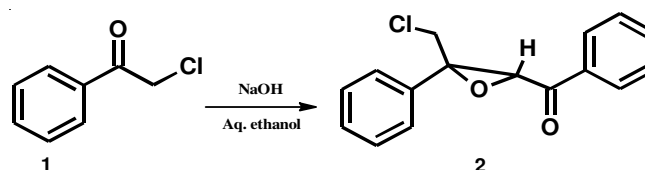
The compound, 3-chloromethyl-(3-phenyl-oxiranyl)phenyl methanone [m.f. C₁₆H₁₃O₂Cl] was a self-condensation product of phenacyl chloride where the reaction carried out in ethanol medium using inorganic base. This was crystalized in monoclinic with space group P2₁/c (no. 14), a = 10.1312 (2) Å, b = 11.7728 Å, c = 11.8566 Å, V = 1344.07 Å³, Z = 4 and ρ_{calc.} = 1.348 mg/mm³. The dihedral angle between two aromatic rings is 73.46 (5). The epoxide ring is oriented at dihedral angles of 62.12 (9°) and 60.87 (7°) with respect to the phenyl and benzoyl rings. The non-classical intermolecular hydrogen bonding of C-H...O type has been observed in the crystal structure of molecule.

Keywords: 3-Chloromethyl-3-phenyl-oxiranyl)phenyl methanone, Crystal structure, New polymorph.

INTRODUCTION

The C-C bond formation is always been well known chemistry for the preparation of new organic compounds with novel various properties. Darzens' reaction is also one of them which used for C-C bond formation in synthetic branch of organic chemistry^{1,2}. This reaction also allows to prepare α,β-epoxy carbonyl derivatives with new stereocenters *via* diastereo-control mechanism. These condensation reactions are carried out in the presence of strong base while organic solvents usually used as medium³. In order to meet the modern methodologies for betterment of environment and more socio-economic benefits phase transfer catalyst (PTC) have also been applied as catalyst⁴⁻⁶. Wang *et al.*⁷ reported the Darzens condensation reaction of ethyl acetate with different aldehydes using newly synthesized polystyrene-based quaternary ammonium compounds as catalysts. The pharmaceutical significance (synthesis of diltiazem; a blood pressure lowering drug) of Darzens reactions vindicates the special consideration of researchers^{8,9}. The epoxy ketones, both in their racemic as well as optically active forms are considered as useful building blocks for the synthesis of various organic compounds¹⁰. The two active functionalities (keto and epoxy) can be further derivatized to yield potential intermediates of natural, industrial and biologically active compounds¹¹⁻¹³. The title compound *i.e.*, 3-chloromethyl-(3-phenyl-oxiranyl)phenyl

methanone is also epoxy ketone and synthesized *via* self-condensation of phenacyl chloride in the presence of sodium hydroxide as base and crystalized in ethanol under slow evaporation, **Scheme-I**. The crystal structure is being reported here as another monoclinic polymorph of 3-chloromethyl-(3-phenyl-oxiranyl)phenyl methanone.



Scheme-I: Synthesis of 3-chloromethyl-(3-phenyl-oxiranyl)phenyl methanone (2)

EXPERIMENTAL

The phenacyl chloride (1 g, 6.47 mmol) was added to aqueous ethanolic solution (1 : 1) of sodium hydroxide (0.52 g, 12.93 mmol) and the mixture was allowed to stir at room temperature for 2 h. The precipitate obtained was filtered off, washed with cold water and recrystallized in ethanol under slow evaporation to obtain a suitable crystal for X-ray diffraction studies. The ¹H NMR was recorded on Bruker Avance 600 MHz spectrometer (Bruker, Germany), in CDCl₃ as solvent. The values

of proton are reported as chemical shifts (δ , ppm) along-with their multiplicity (s, singlet; d, doublet; t, triplet; q quartet) relative to the residual CDCl_3 (7.26 ppm). The melting point was recorded on Stuart scientific SMP3 (Bibby, UK) melting point apparatus and is reported as uncorrected.

^1H NMR (600 MHz) (CDCl_3) δ : 7.89 (2H, d, aromatic), 7.57 (1H, t, aromatic), 7.40 (2H, t, aromatic), 7.35 (2H, q, aromatic), 7.22 (2H, d, aromatic), 7.21 (1H, d, aromatic), 4.65 (1H, s, CH), 4.08 (2H, s, CH_2). m.p. 152-153 °C.

Crystallization of compound **2** in ethanol under slow evaporation gave colorless, block type crystals. A suitable crystal was selected and mounted on an Agilent Super Nova Atlas Dual Source, Agilent Technologies diffractometer using the Crys Alis Pro software¹⁴. The crystal was kept at 296 K during data collection. Using Xseed¹⁵, the structure was solved with the ShelXS¹⁶ structure solution program using direct methods and refined with the ShelXL¹⁶ refinement package using least squares minimization. All the hydrogen atoms were positioned geometrically with $d_{\text{aromatic-H}} = 0.93 \text{ \AA}$, $d_{\text{chiral-H}} = 0.97 \text{ \AA}$ & $d_{\text{methylene-H}} = 0.98 \text{ \AA}$ and were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The figures were drawn with the help of PLATON¹⁷ using WinGX¹⁸. The crystal data was deposited at the Cambridge Crystallographic Data Centre and it has been assigned the deposition number as CCDC 940725. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

The title compound was synthesized through a simple self-condensation using inorganic base and recrystallized in ethanol as a new monoclinic polymorph. The cambridge structural database (CSD)¹⁹ speaks about two other polymorphs²⁰ with codes QECFAF and QECFEJ. The spectroscopic and crystallographic studies were taken out for the characterization of product. According to the ^1H NMR spectra of molecule it is clear that the hydrogen atoms of the benzoyl rings appear in the downfield region [7.89 (2H, d, aromatic), 7.57 (1H, t, aromatic), 7.40 (2H, t, aromatic)] due to the de-shielding effect of carbonyl group. On the other hand, five hydrogen atoms of phenyl ring are appeared at 7.35 (2H, dd, aromatic), 7.22 (2H, d, aromatic) and 7.21 (1H, dd, aromatic). The singlet peak of the hydrogen atom attached to chiral carbon C_2 appeared at 4.65 while the two hydrogen atoms of methylene CH_2 group appeared at 4.08. The Table-1 contains the detail of the crystal data, data collection and structure refinements. Selected bond lengths and bond angles are provided in Tables 2 and 3, respectively. The ORTEP diagram of molecule **2** is shown in Fig. 2, it reveals that the molecule contain two aromatic rings ($\text{C}_4\text{---C}_9$) & ($\text{C}_{10}\text{---C}_{15}$) with root mean square (r.m.s) deviation of 0.0018 (1) $\text{\AA}$ & 0.0033 (1) $\text{\AA}$ of the planes produced from their atoms respectively. The oxirane ring ($\text{C}_1/\text{C}_2/\text{O}_2$) is exactly planer with 0.000 $\text{\AA}$ r.m.s. deviation of its fitted. The three bond angles produced from fitted atoms are 62.78 (8°), 58.39 (8°) and 58.82 (8°).

The dihedral angle between the plane produce through the bonded atoms of two aromatic rings is 73.46 (5°). The oxirane ring is oriented at dihedral angle of 62.12 (9°) and

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **2**

Empirical formula	$\text{C}_{16}\text{H}_{13}\text{O}_2\text{Cl}$
Formula weight	272.71
Temperature (K)	296.15
Crystal System	monoclinic
Space group	$\text{P}2_1/\text{c}$
a ($\text{\AA}$)	10.1312 (2)
b ($\text{\AA}$)	11.7728 (2)
c ($\text{\AA}$)	11.8566 (3)
β (°)	108.116 (3)
Volume ($\text{\AA}^3$)	1344.07 (5)
Z	4
ρ_{calc} , mg (mm^3)	1.348
$F(000)$	568.0
Crystal size (mm^3)	$0.48 \times 0.17 \times 0.08$
2θ range for data collection	9.18 to 152.72°
Index ranges (h, k, l)	$-11 \leq h \leq 12, -14 \leq k \leq 14, -14 \leq l \leq 12$
Reflections collected	12607
Independent reflections	2789 [$R(\text{int}) = 0.0355$]
Data/restraints/parameters	2789/0/173
Goodness-of-fit on F^2	1.053
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0353, wR_2 = 0.0967$
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0392, wR_2 = 0.1014$
Largest diff. peak/hole / $\text{e \AA}^{-3}$	0.20/-0.26

TABLE-2
SELECTED BOND LENGTHS OF COMPOUND **2**

Atom	Atom	Length ($\text{\AA}$)
C11	C16	1.7886(15)
O1	C1	1.4349(15)
O1	C2	1.4284(17)
O2	C3	1.2162(17)
C1	C2	1.4914(19)
C1	C10	1.4955(19)
C1	C16	1.504(2)
C2	C3	1.500(2)
C3	C4	1.4821(19)
C4	C5	1.390(2)
C4	C9	1.386(2)

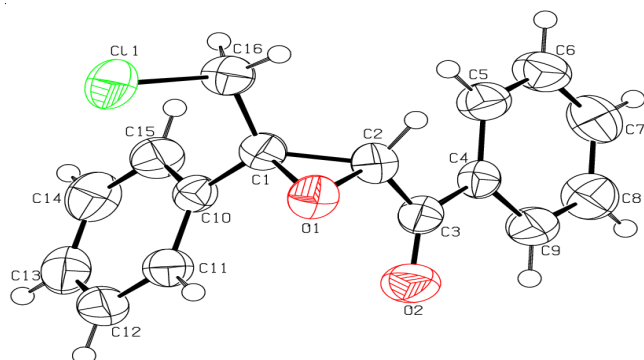
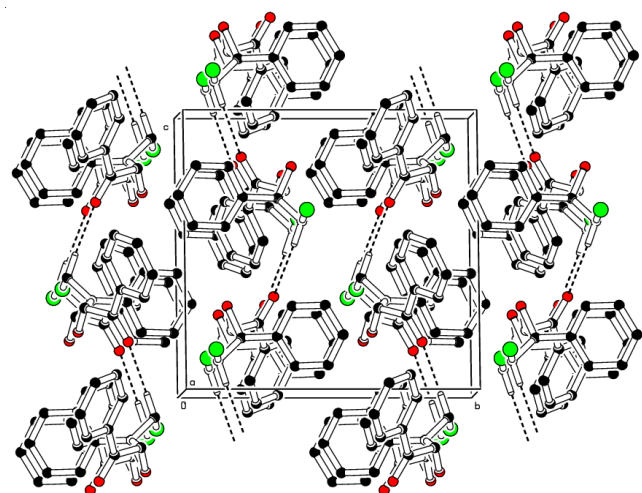
TABLE-3
SELECTED BOND ANGLES OF COMPOUND **2**

Atom	Atom	Atom	Angle (°)
C2	O1	C1	62.78(8)
O1	C1	C2	58.39(8)
O1	C1	C10	115.42(11)
O1	C1	C16	114.29(11)
C2	C1	C10	120.77(11)
C2	C1	C16	115.83(12)
C10	C1	C16	117.96(11)
O1	C2	C1	58.82(8)
O1	C2	C3	117.50(12)
C1	C2	C3	120.21(12)
O2	C3	C2	120.60(13)
O2	C3	C4	121.99(13)
C4	C3	C2	117.42(12)
C5	C4	C3	123.09(13)
C9	C4	C3	118.23(13)

60.87 (7°) with respect to the phenyl ($\text{C}_{10}\text{---C}_{15}$) and benzoyl ($\text{C}_4\text{---C}_9$) rings. The non-classical $\text{C---H}\cdots\text{O}$ type intermolecular hydrogen bonding have also been observed in the molecule which may help to stabilize the crystal structure of molecule Fig. 3 and Table-4. This interaction connects the molecules along c -axes to make an infinite chain.

TABLE-4
HYDROGEN BOND GEOMETRY (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A	Symmetry code / symmetry operation
C ₁₆ -H _{16A} ...O ₂ ⁱ	0.97	2.44	3.3750(19)	160.6	4_565 / 'X, 1/2-Y, Z-1/2

Fig. 2. ORTEP diagram of compound **2** drawn at 50 % probability of thermal ellipsoidFig. 3. Unit cell packing of compound **2** showing the hydrogen bonding using dashed lines, all other hydrogen atoms not involved in hydrogen bonding have been omitted for clarity

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