

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

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Received: 24 July 2013;

Accepted: 6 December 2013;

Published online: 28 April 2014;

AJC-15104

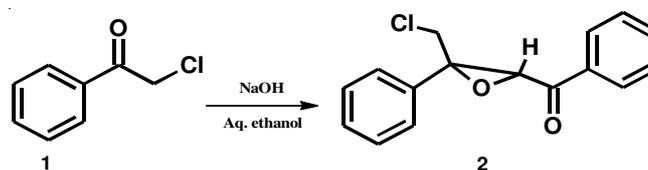
The compound, 3-chloromethyl-(3-phenyl-oxiranyl)phenyl methanone [m.f. C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>Cl] was a self-condensation product of phenacyl chloride where the reaction carried out in ethanol medium using inorganic base. This was crystallized in monoclinic with space group P2<sub>1</sub>/c (no. 14), a = 10.1312 (2) Å, b = 11.7728 Å, c = 11.8566 Å, V = 1344.07 Å<sup>3</sup>, Z = 4 and ρ<sub>calc.</sub> = 1.348 mg/mm<sup>3</sup>. 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<sup>1,2</sup>. 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 medium<sup>3</sup>. 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 catalyst<sup>4,6</sup>. Wang *et al.*<sup>7</sup> 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<sup>8,9</sup>. 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 compounds<sup>10</sup>. The two active functionalities (keto and epoxy) can be further derivatized to yield potential intermediates of natural, industrial and biologically active compounds<sup>11-13</sup>. 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 crystallized 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 <sup>1</sup>H NMR was recorded on Bruker Avance 600 MHz spectrometer (Bruker, Germany), in CDCl<sub>3</sub> as solvent. The values

of proton are reported as chemical shifts ( $\delta$ , ppm) along-with their multiplicity (s, singlet; d, doublet; t, triplet; q quartet) relative to the residual  $\text{CDCl}_3$  (7.26 ppm). The melting point was recorded on Stuart scientific SMP3 (Bibby, UK) melting point apparatus and is reported as uncorrected.

**$^1\text{H NMR}$  (600 MHz) ( $\text{CDCl}_3$ ) $\delta$ :** 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,  $\text{CH}_2$ ). 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 software<sup>14</sup>. The crystal was kept at 296 K during data collection. Using Xseed<sup>15</sup>, the structure was solved with the ShelXS<sup>16</sup> structure solution program using direct methods and refined with the ShelXL<sup>16</sup> 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 PLATON<sup>17</sup> using WinGX<sup>18</sup>. 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](http://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)<sup>19</sup> speaks about two other polymorphs<sup>20</sup> with codes QECFAF and QECFEJ. The spectroscopic and crystallographic studies were taken out for the characterization of product. According to the  $^1\text{H NMR}$  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  $\text{C}_2$  appeared at 4.65 while the two hydrogen atoms of methylene  $\text{CH}_2$  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	$\text{P}2_1/\text{c}$
$\alpha$ (Å)	10.1312 (2)
$\beta$ (Å)	11.7728 (2)
$c$ (Å)	11.8566 (3)
$\beta$ (°)	108.116 (3)
Volume (Å <sup>3</sup> )	1344.07 (5)
Z	4
$\rho_{\text{calc}}$ , mg (mm <sup>3</sup> )	1.348
F(000)	568.0
Crystal size (mm <sup>3</sup> )	0.48 × 0.17 × 0.08
2 $\theta$ range for data collection	9.18 to 152.72°
Index ranges (h, k, l)	-11 ≤ h ≤ 12, -14 ≤ k ≤ 14, -14 ≤ l ≤ 12
Reflections collected	12607
Independent reflections	2789[R(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 / e Å <sup>-3</sup>	0.20/-0.26

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

Atom	Atom	Length (Å)
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 C---H...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 <sub>16</sub> -H <sub>16A</sub> ...O <sub>2</sub> <sup>i</sup>	0.97	2.44	3.3750(19)	160.6	4_565 / 'X, 1/2-Y, Z-1/2

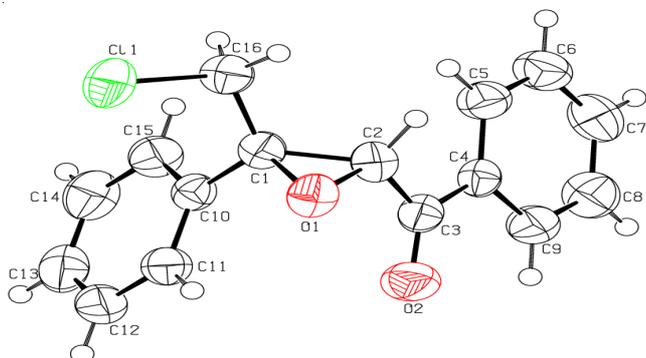


Fig. 2. ORTEP diagram of compound 2 drawn at 50 % probability of thermal ellipsoid

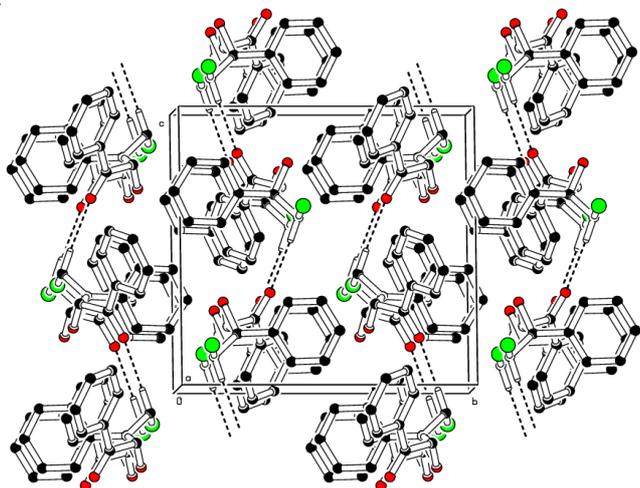


Fig. 3. Unit cell packing of compound 2 showing the hydrogen bonding using dashed lines, all other hydrogen atoms not involved in hydrogen bonding have been omitted for clarity

## ACKNOWLEDGEMENTS

This project was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant no. (169/130/1433). The authors, therefore, acknowledged with thanks DSR technical and financial support.

## REFERENCES

- R.O.C. Norman and C.M. Coxon, Principles of Organic Synthesis, CRC Press, New York (2009).
- R. Noyori, Asymmetric Catalysis in Organic Synthesis, John Wiley & Sons, New York (1994).
- F.W. Bachelor and R.K. Bansal, *J. Org. Chem.*, **34**, 3600 (1969).
- R.K. Boeckman Jr., T.J. Clark and B.C. Shook, *Helv. Chim. Acta*, **85**, 4532 (2002).
- A. Jonczyk and K. Michalski, *Synlett*, 1703 (2002).
- L.W. Xu, J.W. Li, S.L. Zhou and C.G. Xia, *New J. Chem.*, **28**, 183 (2004).
- Z.-T. Wang, L.-W. Xu, C.-G. Xia and H.-Q. Wang, *Helv. Chim. Acta*, **87**, 1958 (2004).
- O. Miyata, T. Shinada, I. Ninomiya and T. Naito, *Tetrahedron*, **53**, 2421 (1997).
- B.M. Adger, J.V. Barkley, S. Bergeron, M.W. Cappi, B.E. Flowerdew, M.P. Jackson, R. McCague, T.C. Nugent and S.M. Roberts, *J. Chem. Soc., Perkin Trans. I*, 3501 (1997).
- C. Lauret, *Tetrahedron Asymm.*, **12**, 2359 (2001).
- J.R. Flisak, K.J. Gombatz, M.M. Holmes, A.A. Jarmas, I. Lantos, W.L. Mendelson, V.J. Novack, J.J. Remich and L. Snyder, *J. Org. Chem.*, **58**, 6247 (1993).
- P.C. Ray and S.M. Roberts, *J. Chem. Soc., Perkin Trans. I*, 149 (2001).
- T. Nemoto, T. Ohshima and M. Shibasaki, *Tetrahedron Lett.*, **41**, 9569 (2000).
- Agilent, CrysAlis PRO, Agilent Technologies, Yarnton, England (2012).
- L.J. Barbour, *J. Supramol. Chem.*, **1**, 189 (2001).
- G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
- A.L. Spek, *Acta Crystallogr. D Biol. Crystallogr.*, **65**, 148 (2009).
- L.J. Farrugia, *J. Appl. Cryst.*, **45**, 849 (2012).
- I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.*, **B58**, 389 (2002).
- P. Bako, E. Czinege, T. Bako, M. Czugler and L. Toke, *Tetrahedron Asymm.*, **10**, 4539 (1999).