Comparative study of the crystal structures of 6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin (C$_{17}$ H$_{13}$ Cl O$_3$) and 2-[6-Chloro-2-oxo-2H- chromen -4-ylmethoxy]-benzonitrile (C$_{17}$ H$_{10}$ Cl N O$_3$)

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Abstract— **4-Phenoxymethylcoumarin by the reaction of 4-bromomethylcoumarin with phenol Compound was subjected to the Claisen rearrangement at high temperature, which gave negative results. Subsequently a number of 4-aryloxymethylcoumarin were synthesised as possible anti-microbial agents. Introduction of biocompatible fragments like vanillin and paracetamol resulted in novel 4-aryloxymethylcoumarins which exhibited anti-inflammatory, analgesic and interesting photophysical properties also.**

The first report on the X-ray diffraction studies on 4-aryloxymethylcoumarins has revealed that the molecules exist as head-tail dimers in solid state as observed in the case of 7-methyl-4-tolyloxymethylcoumarin.

In the light of above observations following 4-aryloxymethylcoumarins possessing chloro/bromo substituents have been subjected to X-ray diffraction studies

Index Terms— **Phenoxymethylcoumarin, crystal x-ray study, Molecular Packing and hydrogen bonding.**

I. INTRODUCTION

The title compound was synthesised by the reaction of 6-chloro-4 bromomethylcoumarin and *p*-cresoland 7-methyl 6, 8-dinitro 4-bromomethyl coumarin. The title compound (. (Fig 1 (a))) was synthesised by the reaction of 6-chloro-4 bromomethylcoumarin and *p*-cresol. [1].

The title compound ((Fig 1 (b))) was synthesised by the reaction of 6-chloro-4 bromomethylcoumarin and salicylonitrile

The compound was purified by routine chemical methods, its observed melting point 240° C. IR/ NMR data was in agreement with literature report [1]. This was used as an intermediate in the synthesis of polycyclic coumarins [2].

II. EXPERIMENTAL

Compound (Fig 4.1.1) has been grown by slow evaporation technique using ethyl acetate. Colorless block like single crystals suitable for X-ray diffraction was obtained. The density of the crystal was measured by flotation technique using potassium iodide solution. The measured density agreed with the calculated density for Z = 4.

Compound (Fig 1 (b)) Compound has been grown by slow evaporation technique using ethanol. Colorless thin plate like single crystals suitable for X-ray diffraction was obtained. The density of the crystal was measured by flotation technique using potassium iodide solution. The measured density agreed with the calculated density for Z =

III.X-RAY DATA COLLECTION

The three dimensional intensity data was collected using a crystal of size $0.30 \times 0.20 \times 0.20$ mm mounted on an Bruker axs kappa apex2 [3] CCD Diffractometer with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) in fine-focused sealed tube at temperature 293(2)K The intensities of reflections 9957 were collected in the 2θ range 1.61 to 26.58°. The data was collected using ω and φ scans mode with h,-5 to 3, k, -11 to 11, and l, 31 to 31.The intensities were collected for Lorentz and polarisation effects. Among the 2137 unique reflections collected, 1502 observed reflections with I $\geq$ 2 σ (I). The space group *P2$_1$/c* assigned from

the systematic absences. The cell parameters are a = 15.3068(5), b = 6.9353(2), c = 14.9566(5) Å and β = 116.923(2)^0. V = 1415.66(8)A$^{\circ 3}$. Multi-scan absorption was carried out using SADABS [4]. The calculated absorption coefficient was 0.277 mm^{-1}. The three dimensional intensity data was collected using a crystal of size 0.23x0.18x0.14 mm mounted on an 'OXFORD DIFFRACTION XCALIBUR-S' Enhance (Mo) X-ray Source' (λ = 0.71073 Å),. At low (150K) temperature. The data was collected using ω and φ scans mode with h,-9 to 9, k, -30 to 28, l, -9 to 8. The intensities were collected for Lorentz and polarisation effects. 10462 measured reflections of which 2388 independent reflections and 1022 reflections with I $\geq$ 2 σ (I). The space group $P\ 2_1/n$ assigned from the systematic absences. The cell parameters refined are a =7.6248(12), b = 25.810(4), c =7.7136(14)Å and β = 116.19(2)°. V = 1360.7(4)A$^{\circ 3}$. Multi-scan absorption was carried out using SADABS [4]. The calculated absorption coefficient was 0.293 mm^{-1}.
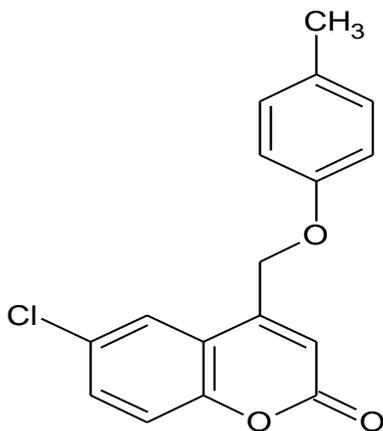

Fig .1 (a)
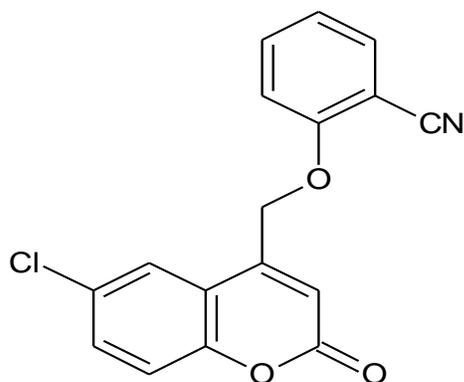

Fig .1 (b)

IV. RESULTS AND DISCUSSIONS

Conformation of molecule
Molecule ((Fig 2 (a))) is planar and individual coumarin and phenoxy moieties are planar. The phenoxy moiety is oriented anti periplanar with respect to the coumarin ring as indicated by the C7-C10-O3-C11 angle of 179.97°. The C10-O3 band is cis with respect to the coumarin ring (C5-C4) double bond is almost eclipsed with the dihedral angle of 5.3° between C8-C7-C10-O3.

Bond lengths and Bond angles
A significant bond deviation is observed at C5-C7 (1.449Å) due to the bridging of α pyrone ring and benzene ring at C5 carbon atom and also a substituent present on C7 carbon atom. This is also reflected at C8-C9 and C7-C10 due to attachment of oxygen atom at C9 carbon atom and a phenoxy group at C10 carbon atom respectively.
A significant bond angle of deviation is observed at C6-C5-C4 (117.91°) this is due to the flexing of α-pyrone ring and benzene ring at C5 and C6 carbon atoms. This is also reflected at C6-C5-C7 (117.61°). Another significant bond angle of deviation is observed at C15-C14-C13 (117.46°) due to presence of electron releasing methyl group on C14 carbon atom which makes repulsion of electrons. One more positive bond angle of deviation observed at C6-O1-C9 due to delocalisation of lone pair of electrons on the O1 atom which is responsible by benzene ring at C6 position and O2 present on C9 carbon atom.
The molecule is stabilised by a number of intermolecular C-H. The molecule shows spatial proximity between H1-Cl1 of 2.880 Å. In addition to these there is a strong C-H…Cl hydrogen bond stabilizes the structure thus forms the sheet like arrangement of the molecules.

Conformation of molecule
The molecule ((Fig 2 (b))) is slightly non planner as indicated by the dihedral angle 16° between the two planes containing coumarin and phenoxy moieties. The phenoxy moiety is oriented with respect to the coumarin ring as indicated by the C7-O1-C8 - C9 angle of 169.05°. The phenoxy moiety is cis with respect to the double bond in the coumarin ring.

Bond lengths and bond angles
Bond length deviations observed C10-C11 (1.4149Å) and C10-C15 (1.3907Å) due to bridging of α pyrone

ring at benzene ring. Bond angle deviation observed at C11-C10-C15 (116.21°) this is due to fusing of α pyrone ring at C10 and C15 also reflected at C13-C14-C15 (117°). Deviation observed at C9-C17-C16 (122.30°) due to attachment of O2 at C16.

There are four molecules in the packing of molecule is governed by number of inter molecular hydrogen bonds such as C-H…N, C-H…O, C-H…Cl hydrogen bonds. The molecule primarily linked via C-H…O interactions and C-H…N hydrogen bonds forming 1-D layers further linked by C-H…Cl

The crystallographic refinement data is given in the Table 1 (a) and 1(b). Comparison of C-Br bond length in 4-bromomethylcoumarins are listed in the Table 2, Comparison of dihedral angle between three structures of 4- Aryloxymethylcoumarins with hydrogen bonding.

Table 3. Comparison of space group, moiety, atom/unit cell and cell parameters between three structures of 4-Aryloxymethylcoumarins

Table.4. Hydrogen bonding geometry of structures of 4-Aryloxymethylcoumarins. Scheme and perspective views of an Ortep plot [5]. of the molecule with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 1 (a) and . Fig. 1 (b) and Fig. 2 (a) and. Fig. 2 (b) respectively
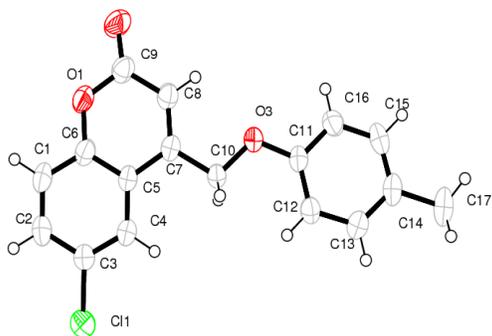
ACKNOWLEDGMENT

Fig.2 (a) 6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.
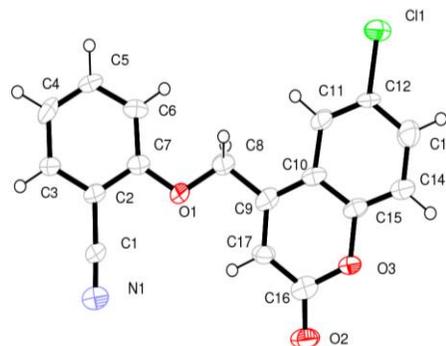

Fig.2 (b) 6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin coumarin *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

Table.1 (a). Crystal data and structure refinement.

DATA	COMPOUND
Empirical formula	$C_{17} H_{13} Cl O_3$
a	15.3068(5) Å
b	6.9353(2) Å
c	14.9566(5) Å
β	116.923(2) °
Volume	1415.66(8) Å^3
Crystal system	Monoclinic
Formula weight	300.72
Space group	*P21/c*
F(000)	624
Radiation	MoKα (λ = 0.71073 Å)
Z	4
Absorption coefficient	0.277 mm^{-1}
Calculated density	1.411 Mg/m^3
No. Parameters	191
R-obs	0.0533
wR$_2$ (all)	0.1387
Theta range for data collection	1.49 to 29.16 °
h $_{min, max}$; k $_{min, max}$; l $_{min, max}$	-20<=h<=20, -9<=k<=6, -20<=l<=20
Max. and min. transmission	0.967 and 0.932
Goof(S)	1.081
No. Unique reflections.	3818
Temperature	293(2) K
Largest diff. peak and hole	0.269 and -0.216 e.A^{-3}

Table.1 (b). Crystal data and structure refinement.

DATA	COMPOUND
Empirical formula	$C_{17} H_{10} Cl N O_3$
a	7.6248(12) Å

b	25.810(4) Å
c	7.7136(14) Å
β	116.31(2) °
Volume	1360.7(4) Å^3
Crystal system	Monoclinic
Formula weight	311.71
Space group	*P* 21/c
F(000)	640
Radiation	MoKα (λ = 0.71073 Å)
Z	4
Absorption coefficient	0.293 mm^{-1}
Calculated density	1.522 Mg/m^3
No. Parameters	199
R-obs	0.2190
wR$_2$ (all)	0.4104
Theta range for data collection	3.23 to 25.00 °
h $_{min, max}$; k $_{min, max}$; l $_{min, max}$	-9<=h<=9, -30<=k<=28, -9<=l<=8
Max. and min. transmission	0.9601 and 0.9357

Goof(S)	1.099
No. Unique reflections.	2388
Temperature	150(2) K
Largest diff. peak and hole	0.9601 and 0.9357e.A^{-3}

Table.2 Comparison of dihedral angle between three structures of 4- Aryloxymethylcoumarins with hydrogen bonding.

Compound	Dihedral Angle(°)	Atoms involved	Contacts
6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin	179.97°.	C7-C10-O3-C11	C-H…O and C-H…Cl
2-[6-Chloro-2-oxo-2H-chromen -4-ylmethoxy]-benzonitrile.	169.05°	C7-O1-C8 - C9	C-H…N, C-H…O and C-H…Cl

Table.3 Comparison of space group, moiety, atom/unit cell and cell parameters between three structures of 4-Aryloxymethylcoumarins

Compound	Space group	system	Z	Cell parameters
6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin	*P2$_1$/c*	Monoclinic	4	*a* = 15.3068(5), *b* = 6.9353(2), *c* = 14.9566(5) Å and β = 116.923(2)^0
2-[6-Chloro-2-oxo-2H- chromen -4-ylmethoxy]-benzonitrile.	*P 2$_1$/c*	Monoclinic	4	*a* =7.6248(12), *b* = 25.810(4), *c* =7.7136(14) Å and β= 116.19(2)^0

Table.4. Hydrogen bonding geometry of structures of of 4-Aryloxymethylcoumarins

Compound	(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°	Symmetry code
6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin	C4-H4…O4^i	0.930(0)	2.691(2)	3.553(2)	154	(i) x,-y+1/2,+z-1/2 (ii) x,-y+1/2,+z+1/2
	C10-10B…O2^i	0.970(0)	2.474(2)	3.303(2)	143	
	C12-12B…O2^i	0.930(0)	2.667(2)	3.402(2)	136	
	C1-H1…Cl^{ii}	0.930(0)	2.880(1)	3.693(1)	145	
6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin	C8-H8A…O2^i	0.990(1)	2.802(7)	3.529(1)	131	(i) x+1,-y,+z+1 (ii) x+1,-y+1/2,+z+1/2 (iii) –x+1, +y+1/2,-z+1/2+1 (iv) x+1, +y,+z+1
	C11-H11…O2^i	0.950(1)	2.620(8)	3.534(1)	161	
	C8-H8B...O2^{ii}	0.990(1)	2.873(6)	3.736(1)	146	
	C11-H1...O2^{ii}	0.990(1)	2.873(6)	3.736(1)	146	
	C3-H3...Cl1^{iii}	0.950(1)	2.895(6)	3.644(1)	136.	
	C5-H5...N1^{iv}	0.950(1)	2.617(6)	3.269(1)	126.	

REFERENCE

[1]. Kulkarni, M. V.; Pujar, B. J.; Patil, V. D. *Arch. Pharm.* (Weinheim). 1983, *316 (1)*, p 15-21.

[2]. Khan, I. A.; Kulkarni, M. V.; Gopal, M.; Shahabuddin, M. S. *Bioorg. Med. Chem. Lett.,* 2005, *15*, p 3584-3587.

[3]. Bruker (2004). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

[4]. Sheldrick, G. M. 2008. Acta Cryst. A64, p 112-122.

[5]. Farrugia, L. J. (1997). J. Appl. Cryst. 30, p 565.