Crystal structure of 4-(4-Bromo-phenoxymethyl)-5, 7-dimethyl-chromen-2-one ($C_{18}H_{15}BrO_3$)

Ramakrishna Gowda [1], K.V Arjuna Gowda [2]
[1] *Department of Physics, Government College for Women, Kolar, India*
[2] *Departments of Physics and PG Center, Government First Grade College, Hosakote, Bangalore*

Abstract **- 4-Phenoxymethylcoumarin was reported by 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-aryloxymethylcoumarins were synthesised as possible anti-microbial agents Introduction of biocompatible fragments like vanillin and paracetamol resulted in novel 4-aryloxymethylcoumarins and 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 **- Bromo, Dimethyl, crystal x-ray study, Molecular Packing and hydrogen bonding.**

I.INTRODUCTION

The title compound was synthesised by the reaction of 5,7-dimethyl-4 - bromomethylcoumarin and 4-bromophenol The compound was purified by routine chemical methods, its observed melting point 260° C. IR/ NMR data was in agreement with literature report [1].

II. EXPERIMENTAL

Compound (Fig .1) has been grown by slow evaporation technique using Dioxane. Colorless 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 = 4.

III.X-RAY DATA COLLECTION

The three dimensional intensity data was collected using a crystal of size 0.1x0.2x0.2 mm mounted on an Bruker SMART APEX II [2] diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) in fine-focused sealed tube at temperature 293(2)K The intensities of reflections 8129 were collected in the 2θ range 1.857-26.371^0.The data was collected using ω and φ scans mode. With h,-10 to 10, k, -10 to 10, l, -10 to 14. Among 8129 measured reflections, 3103 independent reflections and 2301 reflections with $I \geq 2\ \sigma$ (I). The space group $P\ \bar{1}$ assigned from the systematic absences. The cell parameters refined are a = 8.3902, b = 8.7771, c = 11.6380 Å and $\beta = 72.889(2)^0$. V=762.20(16)Å^3 .With multi scan absorption correction. Multi-scan absorption was carried out using SADABS [2]. The calculated absorption coefficient was 2.706 mm^{-1}

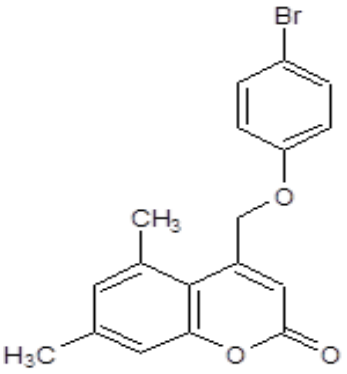

Fig .1

Structure solution and Refinement

The structure was solved by direct methods using SHELXS-97 [3]. The position of all non-hydrogen atoms were revealed in the best E-map. Then refined

using the program SHELXL-97 [3] by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R (F) = 0.0746, *w*R(F^2) = 0.1103. The difference Fourier map further revealed all H-atoms. All the hydrogen atoms parameters were included in the final steps of with weight assigned to a structure factor calculation using the scheme w =1/ [σ^2 (Fo^2) + $(0.1851P)^2$+5.624P] where P= (Fo^2+2Fc^2)/3. The parameters at the end of final refinement were R (F) = 0.042, *w*R(F^2) = 0.126. The minimum and maximum electron densities from difference Fourier map are -0.37 and 0.74 e.A^{-3} respectively.

IV. RESULTS AND DISCUSSIONS

The crystallographic refinement data is given in the Table 1.The bond lengths and bond angles for non-hydrogen atoms are listed in the Table 2 and Table 3. The Table 4. gives torsion angles involving non-hydrogen atoms. A perspective view of a Ortep plot of the molecule with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 1. Fig.2 shows packing of molecules [4] with C-H…O Fig .3 shows the single molecule in a unit cell. contacts and the packing of the molecule in the unit cell [5].. The least square planes and dihedral angles are listed in Table 5. Hydrogen bonding geometry listed in Table 6.

Conformation of the molecule

The entire molecular is planar the phenoxy moiety is anti-periplanar with respect to the coumarin as indicated by the C10-05-C10-07 dihedral angle of 177.53°. The phenoxy moiety is oriented cis with respect to the double bond in the coumarin ring and is eclipsed as reveled by O3-C10-C7-C8 dihedral angle of 3.17°.

Bond lengths and angles

There is a significance deviation in bond angle at 01-C5-C4 (114.2(4) °) due to the electronic repulsion of oxygen (02) atom which is present at C9 carbon tom. This is also reflected at C7- C8- C9 (123.8(4) °) and C5 - O1 - C9 (122.8(3) °) but these are due to fusing the benzene ring with α pyrone ring. Another significant bond angle of deviation is observed at C2-C3-C4 (117.87°) due to presence of electron eleasing methyl group on C_{18} carbon atom which makes repulsion of electrons.

It is important to note that due to the stoic effect of the two methyl group at C5 and C7 the number of molecular per unit cell is 2 which is also reflected in different modes of packing. The molecules oriented parallel to each other as shown in Fig 3. The molecule indicate Br….Br interactions (Br1-Br1=3.594Å).The molecule is stabilised by a number of intermolecular C-H…O (Fig 2) hydrogen bonds listed in table 4.3.6c

V.ACKNOWLEDGMENT

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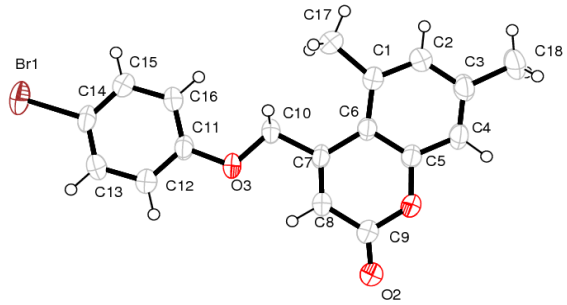

Fig.1 *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

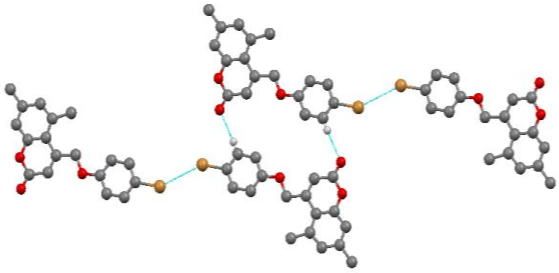

Fig. 2. Packing diagram showing C-H…O and Br-Br contacts

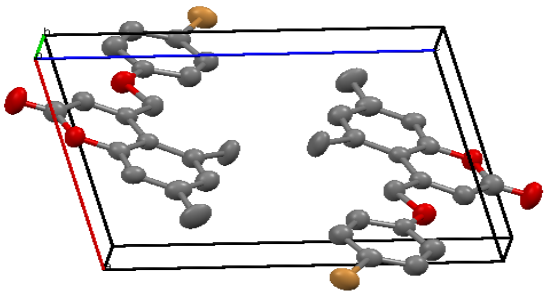

Fig. 3. Packing diagram viewed down b-axis.

Table.1. Crystal data and structure refinement.

DATA	COMPOUND
Empirical formula	C_{18} H_{15} Br_1 O_3
a	8.3902(10) Å
b	8.7771(11) Å
c	11.6380(14) Å
β	72.889(2) °
Volume	762.20(16) $Å^3$
Crystal system	Triclinic
Formula weight	359.22
Space group	P $\bar{1}$
F(000)	334
Radiation	MoKα
Z	2
Absorption coefficient	2.706 mm^{-1}
Calculated density	1.57 Mg/m^3
No. Parameters	199
R-obs	0.042
wR_2 (all)	0.126
Theta range for data collection	1.857-26.371°
$h_{min, max}$; $k_{min, max}$; $l_{min, max}$	-10-10,-10-10,-14-14
Max. and min. Transmission	0.6014 and 0.5343
Goof(S)	0.995
No. Unique reflections.	2106
Temperature	293k
Largest diff. peak and hole	0.37 and 0.74 $e.A^{-3}$

Table 2.List of Bond lengths (Å), esd's given in the parentheses

Atom1-atom2	Angle
Br(1) - C(14)	1.912(4)
C(5) - C(6)	1.413(6)
C(5) - C(4)	1.384(6)
C(5) - O(1)	1.373(5)
C(6) - C(7)	1.466(6)
C(6) - C(1)	1.410(6)
C(7) - C(8)	1.328(6)
C(7) - C(10)	1.515(5)
C(4) - C(3)	1.366(7)
C(2) - C(1)	1.384(6)
C(2) - C(3)	1.396(6)
C(9) - C(8)	1.452(6)
C(9) - O(1)	1.374(6)
C(9) - O(2)	1.190(6)
C(1) - C(17)	1.516(6)
C(3) - C(18)	1.514(6)
C(14) - C(15)	1.366(7)
C(14) - C(13)	1.364(7)
C(15) - C(16)	1.392(6)
C(10) - O(3)	1.418(5)
C(11) - C(16)	1.373(7)
C(11) - C(12)	1.380(6)
C(11) - O(3)	1.384(5)
C(12) - C(13)	1.393(6)

Table 3. List of Bond angles (º), esd's given in the parentheses

Atom1-atom2-atom3	Angle
C(6) - C(5) - C(4)	123.3(4)
C(6) - C(5) - O(1)	122.5(4)
C(4) - C(5) - O(1)	114.2(4)
C(5) - C(6) - C(7)	115.3(4)
C(5) - C(6) - C(1)	116.3(4)
C(7) - C(6) - C(1)	128.4(4)
C(6) - C(7) - C(8)	120.3(4)
C(6) - C(7) - C(10)	120.4(4)
C(8) - C(7) - C(10)	119.3(4)
C(5) - C(4) - C(3)	119.9(4)
C(1) - C(2) - C(3)	123.6(5)
C(8) - C(9) - O(1)	115.3(4)
C(8) - C(9) - O(2)	127.2(5)
O(1) - C(9) - O(2)	117.4(4)
C(6) - C(1) - C(2)	119.0(4)
C(6) - C(1) - C(17)	125.0(4)
C(2) - C(1) - C(17)	116.0(4)
C(4) - C(3) - C(2)	117.8(4)
C(4) - C(3) - C(18)	121.9(5)
C(2) - C(3) - C(18)	120.3(5)
C(7) - C(8) - C(9)	123.8(4)
C(5) - O(1) - C(9)	122.8(3)
Br(1) - C(14) - C(15)	118.2(4)
Br(1) - C(14) - C(13)	119.4(4)
C(15) - C(14) - C(13)	122.4(4)
C(14) - C(15) - C(16)	119.2(5)
C(7) - C(10) - O(3)	109.6(4)
C(16) - C(11) - C(12)	120.4(4)
C(16) - C(11) - O(3)	124.2(4)
C(12) - C(11) - O(3)	115.4(4)
C(15) - C(16) - C(11)	119.5(4)
C(11) - C(12) - C(13)	120.2(5)
C(14) - C(13) - C(12)	118.3(4)
C(10) - O(3) - C(11)	115.6(3)

Table 4. List of Torsion angles (º), esd's given in the parentheses

Atom1-atom2-atom3-atom4	Angle
Br1 -C14 -C15 -C16	-178.64
C13 -C14 -C15 -C16	1.17
Br1 -C14 -C13 -C12	178.91
C15 -C14 -C13 -C12	-0.89

C14 -C15 -C16 -C11	-0.60
C14 -C13 -C12 -C11	0.05
C18 -C3 -C2 -C1	-179.35
C4 -C3 -C2 -C1	1.05
C18 -C3 -C4 -C5	-179.24
C2 -C3 -C4 -C5	0.35
C3 -C2 -C1 -C17	177.44
C3 -C2 -C1 -C6	-1.86
O2 -C9 -O1 -C5	179.58
C8 -C9 -O1 -C5	-2.79
O2 -C9 -C8 -C7	177.50
O1 -C9 -C8 -C7	0.14
C3 -C4 -C5 -O1	178.53
C3 -C4 -C5 -C6	-0.93
C15 -C16 -C11 -C12	-0.21
C15 -C16 -C11 -O3	178.37
C9 -O1 -C5 -C4	-176.76
C9 -O1 -C5 -C6	2.71
C9 -C8 -C7 -C6	2.56
C9 -C8 -C7 -C10	-176.79
C2 -C1 -C6 -C5	1.21
C2 -C1 -C6 -C7	-178.06
C17 -C1 -C6 -C5	-178.02
C17 -C1 -C6 -C7	2.71
C4 -C5 -C6 -C1	0.13
C4 -C5 -C6 -C7	179.49
O1 -C5 -C6 -C1	-179.29
O1 -C5 -C6 -C7	0.08
C13 -C12 -C11 -C16	0.49
C13 -C12 -C11 -O3	-178.21
C1 -C6 -C7 -C8	176.67
C1 -C6 -C7 -C10	-3.99
C5 -C6 -C7 -C8	-2.61
C5 -C6 -C7 -C10	176.73
C8 -C7 -C10 -O3	3.17
C6 -C7 -C10 -O3	-176.18
C16 -C11 -O3 -C10	1.16
C12 -C11 -O3 -C10	179.80
C7 -C10 -O3 -C11	-177.53

Table 5 Dihedral angles formed by LSQ-planes

Plane – Plane	Angle (°.)
1 2	2.84(0)
1 3	2.25(0)
2 3	5.08(0)

Table.6.Hydrogen bonding geometry.

(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°
C13-H131 ...O2^{i}	0.932(0)	2.434(0)	3.358(2)	171

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