Comparative study of the crystal structure of 4-bromomethylcoumarins with different groups in the benzene ring

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Abstract **- 4-Bromomethylcoumarins were first reported by Dey and co-workers by the reaction of various phenols and 4-bromoethylacetoacetate under Pechmann cyclisation conditions .Compounds have been used for the synthesis of a variety of ethers, amines, sulphides, bi- and tri-heterocycles which have been screened for anti-microbials, anti-inflammatory and analgesic activities Halomethylcoumarins were screened for their protease inhibiting property and due to the biochemical importance of 7-methoxy-4-bromomethylcoumarin is now commercially available. FT-IR-Raman spectral studies along with ab-initio calculations have indicated the existence of conformers which differ in their orientation with respect to the coumarin ring.**
It is likely that the allylic bromine (with respect to C3-C4 double bond) is oriented an angle of around 100o to the mean plane of the coumarin moiety.
In view of this, it was thought of considerable interest to study the X-ray structures of various 4-bromomethylcoumarins with different groups in the benzene ring.

Index Terms **- bromomethylcoumarin, Methoxy crystal x-ray study, Molecular Packing and hydrogen bonding.**

I.INTRODUCTION

4-Bromomethylcoumarinswere first reported by Dey and co-workers by the reaction of various phenols and 4-bromoethylacetoacetate under Pechmann cyclisation conditions [1]. The results of the following compounds 6-Methoxy-4-bromomethylcoumarin (Fig 1 (a)) and 7,8-Dimethyl-4-bromomethylcoumarin (Fig 1 (b)) have been included..

The compound (Fig 1 (a)) was prepared by the reaction of methoxyphenol and 4 - bromoethylacetoacetate using sulphuric acid as the condensing agent.

The so obtained 6-methoxy-4-bromomethylcoumarin was crystallised from acetic acid, melting point 175^0 C. The spectral data was in agreement with the literature report [2, 3].

The present compound (Fig 1 (b)) was prepared by the reaction of 2, 3-dimethylphenol and 4-bromoethylacetoacetate using sulphuric acid as the condensing agent.

The so obtained 7, 8-dimethyl-4-bromomethylcoumarin was crystallised from acetic acid, melting point 166 $^{\circ}$C. Further the formation of the product was supported by its spectral data.

II. EXPERIMENTAL

Compound (Fig 1 (a)) has been grown by slow evaporation technique using acetic acid. Colorless needle 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)) has been grown by slow evaporation technique using acetic acid. 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 = 8.

III.X-RAY DATA COLLECTION

The three-dimensional intensity data Fig .1 (a) was collected using a crystal of size 0.25 × 0.15 × 0.1 mm mounted on an Bruker axs kappa APEX 2 [4] CCD Diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) in fine-focused sealed tube at temperature 293(2)K

The three-dimensional intensity data Fig .1 (b)

was collected using a crystal of size 0.30 × 0.20 × 0.20 mm mounted on an Bruker axs kappa APEX 2 [4] CCD Diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) in fine-focused sealed tube at temperature 293(2)K

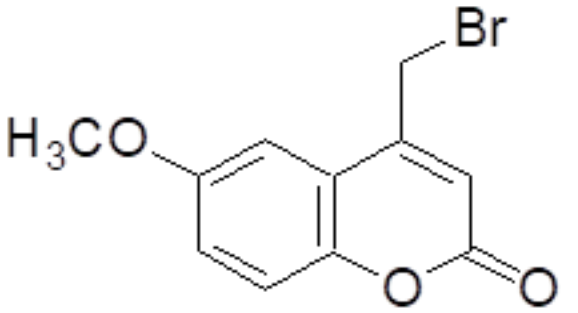

Fig .1 (a)

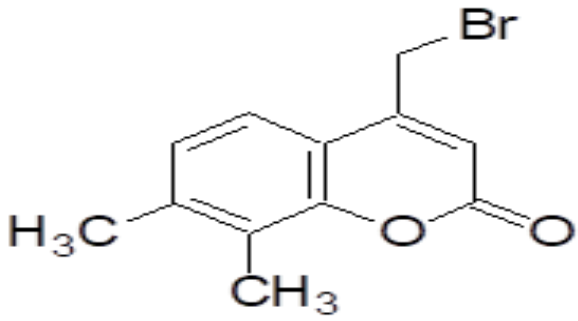

Fig .1 (b)

IV. RESULTS AND DISCUSSIONS

The present investigation has been carried out to understand the influence of various substituents (bromo) on the conformation of 4-Bromomethylcoumarins In the compounds halogenated groups were substituted at different positions. It is observed that the changes in the bond lengths are due to resonance effects, which also accounts for aromaticity. The planarity of the molecule is unaltered due to different substituents coumarin ring.

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-bromomethylcoumarins listed in the Table 3. Comparison of space group, moiety, atom/unit cell and cell parameters between three structures of 4-bromomethylcoumarins given in the Table 4. . Hydrogen bonding geometry of structures of 4-bromomethylcoumarins. Listed in Table 4. Scheme and perspective views of a Ortep plot 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

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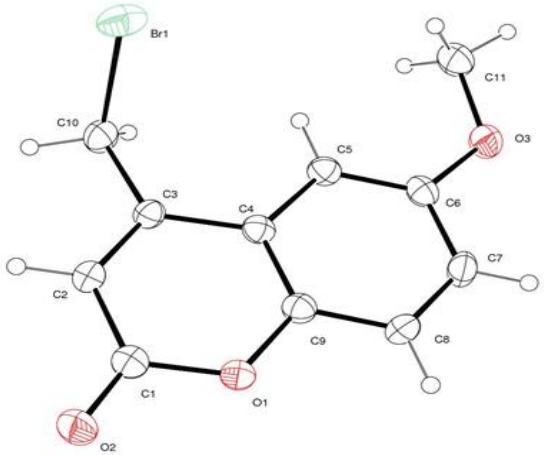

Fig.2 (a) 6-Methoxy-4-bromomethylcoumarin *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms

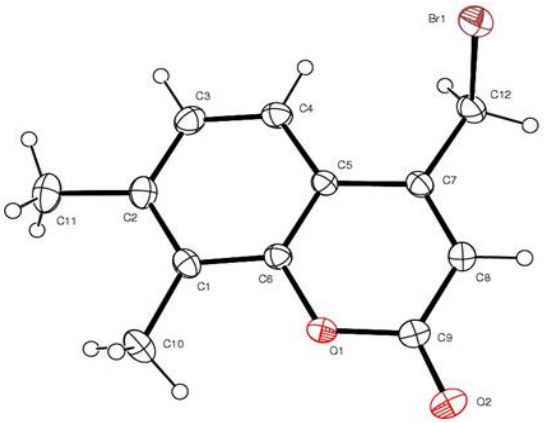

Fig.2 (b) 7,8-Dimethyl-4-bromomethylcoumarin *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

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

DATA	COMPOUND
Empirical formula	C_{11} H_9 Br O_3
a	4.3573(3) Å
b	9.2859(6) Å
c	25.2677(17) Å

β	91.927(3) °
Volume	1021.79 (12) A ° 3
Crystal system	Monoclinic
Formula weight	269.09
Space group	*P 2₁/n*
F(000)	536
Radiation	Mo K_α (λ = 0.71073 Å)
Z	4
Absorption coefficient	4.005 mm^{-1}
Calculated density	1.749 Mg/m^3
No. Parameters	137
R-obs	0.0449
wR_2 (all)	0.1103
Theta range for data collection	1.61° to 26.58°
h min, max; k min, max; l min, max	-5<=h<=3, -11<=k<=11, -31<=l<=31
Max. and min. Transmission	0.5014 and 0.4343
Goof(S)	1.043
No. Unique reflections.	2130
Temperature	293(2) K
Largest diff. peak and hole	0.968 and -0.326 $e.A^{-3}$

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

DATA	COMPOUND
Empirical formula	C_{12} H_{11} Br O_2
a	18.5025(14) Å
b	9.8785(7) Å
c	13.1639(10) Å
β	118.908(2) °
Volume	2106.3(3) A^3
Crystal system	Monoclinic
Formula weight	267.12
Space group	*C2/c*
F(000)	1072
Radiation	Mo K_α (λ = 0.71073 Å)
Z	8
Absorption coefficient	3.878 mm^{-1}
Calculated density	1.685 Mg/m^3
No. Parameters	138
R-obs	0.0676
wR_2 (all)	0.1160
Theta range for data collection	2.41° to 31.85°
h min, max; k min, max; l min, max	-27<=h<=27,-14<=k<=14, 9<=l<=13
Max. and min. transmission	0.571 and 0.432
Goof(S)	1.054
No. Unique reflections.	3610
Temperature	293(2) K
Largest diff. peak and hole	1.780 and -0.727 $e.A^{-3}$

Table.2 Comparison of C-Br bond length in 4-bromomethylcoumarins

Compound	Atoms involved	C-Br (Å)	C-Br (Å) From ab initio calculation [5]
6- Methoxy-4-bromomethylcoumarin	C10-Br1	1.9463(1)	1.963
7, 8-Dimethyl-4-bromomethylcoumarin	C12-Br1	1.9589(2)	

Table.3 Comparison of dihedral angle between three structures of 4- bromomethylcoumarins

Compound	Dihedral Angle(°)	Type of formation	Atoms involved
6- Methoxy-4-bromomethylcoumarin	106	Gauche	C2-C3-C10-Br
7, 8-Dimethyl-4-bromomethylcoumarin	101	Gauche	C8-C7-C12-Br

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

Compound	Space group	Moiety	Z	Cell parameters
6- Methoxy-4-bromomethyl coumarin	*P 2₁/n*	6-Methoxy	4	*a* = 4.3573(3), *b* = 9.2859(6), *c* = 25.2677(17) Å and β = $91.927(3)^0$
7, 8-Dimethyl-4-bromomethyl coumarin	*C2/c*	7,8-Dimethyl	8	*a* = 18.5025 (14), *b* = 9.8785 (7), *c* = 13.1639 (10) Å and β = $118.908\ (2)^0$

Table.5. Hydrogen bonding geometry of structures of 4-bromomethylcoumarins.

Compound	(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°	Symmetry code
4-bromomethylcoumarin	C2 -H2...O1	0.93(0)	2.598(0)	3.450(0)	152	-x+1/2,+y-1/2, -z+1/2+1,
	C2-H2 ...O2	0.93(0)	2.576(0)	3.446(0)	155	-x+1/2,+y-1/2,-z+1/2+1,
	C10-H10A...O2	0.97(0)	2.572(0)	3.437(0)	148	-x+1/2,+y-1/2,

						-z+1/2+1,
	C8 -H8 ...O2	0.93(0)	2.563(0)	3.433(0)	156	-x+1/2,+y+1/2, -z+1/2+1
7, 8-Dimethyl-4-bromomethylcoumarin	C10-H10A…O1	0.96(0)	2.393(0)	3 .751(0)	101	-
	C12-H12B…O2	0.97(0)	2.403(0)	3.342(0)	163	-x+1/2,+y+1/2, -z-1/2.

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