Comparative study of the crystal structures of 7, 8-Dimethyl-4-bromomethylcoumarin ($C_{12}H_{11}BrO_2$) and 7-methyl 6, 8-dinitro 4-bromomethyl coumarin($C_{11}H_7BrN_2O_6$)

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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 100^o 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, Methoxycrystal 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 7,8-Dimethyl-4-bromomethylcoumarin (Fig 1 (a)) and 7-methyl 6, 8-dinitro 4-bromomethyl coumarin (Fig 1 (b)) have been included..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 (a)) 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.

The present (Fig 1 (b)) compound was prepared by the reaction of m-cresol (3-methyl phenol) and 4-bromoethylacetoacetate using sulphuric acid as the condensing agent, followed by nitration of the resulting 7-methyl-4-bromomethylcoumarin.

The so obtained 7-methyl-6, 8-dinitro-4-bromomethylcoumarin was crystallisedfrom acetic acid, melting point 183.4ºC. 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 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.

Compound (Fig 1 (b))) has been grown by slow evaporation technique using ethanol. 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 = 8.

III.X-RAY DATA COLLECTION

The three dimensional intensity data **Fig .1 (a)**was collected using a crystal of size 0.30 × 0.20 × 0.20 mm mounted on an Brukeraxs kappa APEX 2 [4] CCD Diffractometer with graphite monochromated Mo-K_α 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 0.2 × 0.2 × 0.1 mm mounted on an Enraf-Nonius CAD4 [7] diffractometer with Mo K α (λ = 0.71069Å)radiation temperature 293(2) K

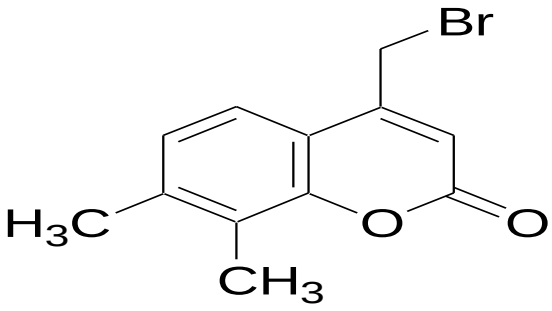

Fig .1 (a)

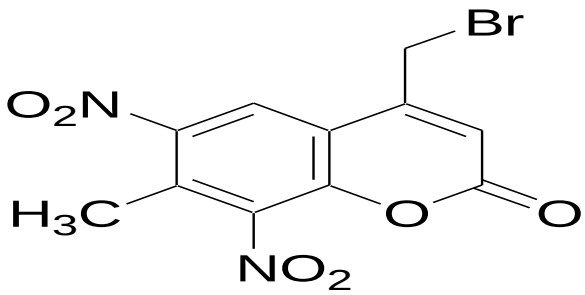

Fig .1 (b)

IV. RESULTS AND DISCUSSIONS

The present investigation has been carried out to understand the influence of various substituents (bromo) on the conformation of 4-BromomethylcoumarinsIn 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-bromomethylcoumarinsare listed in the Table 2, Comparison of dihedral angle between three structures of 4-bromomethylcoumarinslisted 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 moleculewith 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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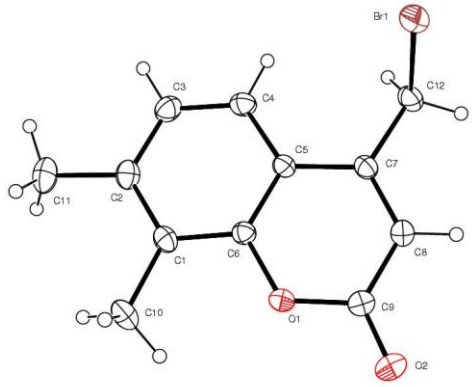

Fig.2 (a) 7, 8-Dimethyl-4-bromomethylcoumarin *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

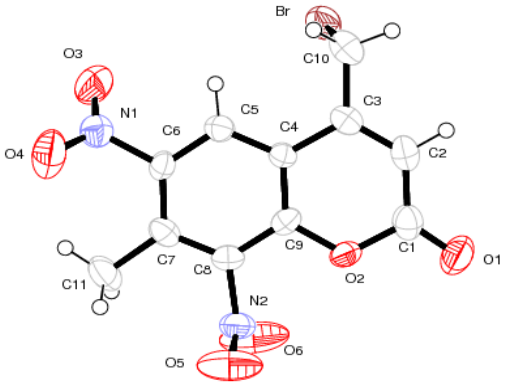

Fig.2 (b) 7-methyl 6, 8-dinitro 4-bromomethyl coumarin *ORTEP*diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

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

DATA	COMPOUND
Empirical formula	C_{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.1 (b). Crystal data and structure refinement

DATA	COMPOUND
Empirical formula	C_{11} H_7 N_2 O_6 Br
a	8.122(2) Å
b	11.091(4) Å
c	27.723(6) Å
β	90°
Volume	2497.3(12) $Å^3$
Crystal system	Orthorhombic
Formula weight	343.09
Space group	*Pbca*
F(000)	1360
Radiation	Mo K_α (λ = 0.71069Å)
Z	8
Absorption coefficient	3.32 mm^{-1}
Calculated density	1.8250 Mg/m^3
No. Parameters	182
R-obs	0.060
wR_2 (all)	0.171
Theta range for data collection	10-15°
h $_{min, max}$; k $_{min, max}$; l $_{min, max}$	0-9,0-13,0-32.
Max. and min. transmission	0.63 -0.82
Goof(S)	1.005
No. Unique reflections.	2196
Temperature	294 K

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

Compound	Atoms involved	C-Br (Å)	C-Br (Å) From ab initio calculculation[5]
7, 8-Dimethyl-4-bromomethylcoumarin	C12-Br1	1.9589(2)	1.963
7-methyl 6, 8-dinitro 4-bromomethylcoumarin	C10-Br	1.9618(8)	

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

Compound	Dihedral Angle(°)	Type of formation	Atoms involved
7, 8-Dimethyl-4-bromomethylcoumarin	101	Gauche	C8-C7-C12-Br
7-methyl 6, 8-dinitro 4-bromomethylcoumarin	104.61	Gauche	C2-C3-C10-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

7, 8-Dimethyl-4-bromomethylcoumarin	*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
7-methyl 6, 8-dinitro 4-bromomethylcoumarin	*Pbca*	7-methyl 6, 8-dinitro	8	*a* = 18.5025 (14), *b* = 9.8785 (7), *c* = 13.1639 (10) Å, and β = 118.908^0

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
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.
7-methyl 6, 8-dinitro 4-bromomethylcoumarin	C11-H11A…O5	0.960(9)	2.887(8)	3.604(11)	132	-x+1/2+1,+y-1/2,+z
	C11-11B…O5	0.960(8)	2.586(8)	3.431(12)	147	-x+1,-y,-z+1

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