Comparative Study of the Crystal Structures of Crystal Structure of 2- [6-Chloro-2-Oxo-2h-Chromen -4-Ylmethoxy]-Benzonitrile. (C₁₇ H₁₀ Cl N O₃). and 4-(4-Bromo-Phenoxymethyl)-5, 7-Dimethyl-Chromen-2-One (C₁₈ H₁₅ Br O₃)

Section A-Research Paper

COMPARATIVE STUDY OF THE CRYSTAL STRUCTURES OF CRYSTAL STRUCTURE OF 2- [6-CHLORO-2-OXO-2H-CHROMEN -4-YLMETHOXY]-BENZONITRILE. ($C_{17} H_{10}$ CL N O_3). AND 4-(4-BROMO-PHENOXYMETHYL)-5, 7-DIMETHYL-CHROMEN-2-ONE ($C_{18} H_{15}$ BR O_3)

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ABSTRACT

4-Phenoxymethylcoumarin was synthesized 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 synthesized as possible anti-microbial agents. Introduction of biocompatible fragments like vanillin and paracetamol resulted in novel 4-aryloxymethylcoumarins V and VI which exhibited anti-inflammatory, analgesic and interesting photo physical 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.

Keywords: Chromen, benzonitrile, phenoxymethyl, crystal x-ray study, Molecular Packing and hydrogen bonding.

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INTRODUCTION

The title compound (I) 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 [1-4]. This was used as an intermediate in the synthesis of polycyclic coumarins [5-8]. The title compound (II) was one of the series of compounds which were screened for their in vitro antitumor activity against human tumor cell lines. 2 – Aminothiazole is an important pharmacophoric moiety occurring in many sulpha drugs. The crystal structure of the compound has been determined to study the point of interest in the structure of this molecule is the orientation of the ester moiety with respect to the thiazole ring. The title compound (II) 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 [3].

MATERIALS AND METHODS

2-[6-Chloro-2-oxo-2H- chromen -4-ylmethoxy]-benzonitrile. (C₁₇ H₁₀ Cl N O₃). and 4-(4-Bromo-phenoxymethyl)-5, 7-dimethyl-chromen-2-one (C₁₈ H₁₅ Br O₃) were synthesized in Department of Physics, Government First Grade College Yelahanka, Bengaluru, Karnataka, India as per the designed scheme.

EXPERIMENTAL & CRYSTALLIZATION

Compound (Fig 4.2.1) 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 = 4.

Compound (Fig 4.3.1) 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.

X-RAY DATA COLLECTION

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 NSCXRD, Indian Institute of Technology Bombay, Mumbai, India. 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 ≥ 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°³. Multi-scan absorption was carried out using SADABS [9]. The calculated absorption coefficient was 0.293 mm⁻¹.

The three-dimensional intensity data was collected using a crystal of size 0.1x0.2x0.2 mm mounted on an Bruker SMART APEX II [9] diffractometer with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) in fine-focused sealed tube at temperature 293(2)K at SSCU, Indian Institute of Science, Bangalore, India. The intensities of reflections 8129 were collected in the 2θ range 1.857-26.371⁰. 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 ≥ 2 σ (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 β = 72.889(2)⁰. V=762.20(16)Å³ with multi scan absorption correction. Multi-scan absorption was carried out using SADABS [9]. The calculated absorption coefficient was 2.706 mm⁻¹

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SHELXS-97 [14]. The position of all non-hydrogen atoms was revealed in the best E-map. Then refined using the program SHELXL-97 [14] by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R (F) = 0.0560, wR(F²) = 0.1349. 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 calculations using the scheme w=1/[σ^2(Fo²)+(0.0732P)²+0.6587P] where P= (Fo²+2Fc²)/3. The parameters at the end of final refinement were R (F) = 0.0497, wR(F²) = 0.1290. The minimum and maximum electron densities

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from difference Fourier map are 0.698 and -0.589 e.A^{-3} respectively.

The structure was solved by direct methods using SHELXS-97 [14]. The position of all non-hydrogen atoms was revealed in the best E-map. Then refined using the program SHELXL-97 [14] by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R (F) = 0.0391, wR(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 calculations using the scheme w=1/[σ^2(Fo^2) + (0.064P) ^{2}+0.000P] where P= (Fo^2+2Fc^2)/3. The parameters at the end of final refinement were R (F) = 0.0537, wR(F^2) = 0.1031. The minimum and maximum electron densities from difference Fourier map are -0.531 and 0.909 e.Å^{-3} respectively.

RESULTS AND DISCUSSION
The crystallographic refinement data is given in Table.1. The bond lengths and bond angles for non-hydrogen atoms are listed in Table 2(Ia), 2(Ib) and 2(IIa), 2(IIb). Table (3 I) and (3 II) Dihedral angles formed by LSQ-planes. The distance and angles between the atoms involved in inter-molecular hydrogen bonding are listed in Table 4 I and 4 II.

Fig 1 Scheme of the title compound I and II, **Fig 2** A perspective view of plot of the molecule (ORTEP-3) with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 2 of I and II and packing of the molecules in the unit cell [15] viewed down b-axis is shown in Fig. 3. The least square planes and dihedral angles are listed in Table 3(a) and Table 3(b) respectively.

Conformation of molecule
The crystallographic refinement data is given in Table 4.2.1. The fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 4.2.2. Anisotropic displacement parameters for non-hydrogen atoms are given in Table 4.2.3. The bond lengths and bond angles for non-hydrogen atoms are listed in Table 4.2.4(a), 4.2.4(b). Table 4.2.5 gives torsion angles involving non-hydrogen atoms [11]. A perspective view of plot of the molecule [12] with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 4.2.2, Fig. 4.2.3 shows packing with C-H…O contacts and packing of the molecules in the unit cell [13] viewed down b-axis is shown in Fig. 4.2.4. The least square planes and dihedral angles [14] are listed in Table 4.2.6(a) and Table 4.2.6(b) respectively. The distance and angles between the atoms involved in intra and inter-molecular hydrogen bonding are listed in Table 4.2.6(c).

Table 1: Crystal data and structure refinement

DATA	COMPOUND I	COMPOUND II
Empirical formula	$C_{17}H_{10}Cl\,N\,O_3$	$C_{18}H_{15}Br_1\,O_3$
a	7.6248(12) Å	8.3902(10) Å
b	25.810(4) Å	8.7771(11) Å
c	7.7136(14) Å	11.6380(14) Å
β	116.31(2) °	72.889(2) °
Volume	1360.7(4) Å^3	762.20(16) Å^3
Crystal system	Monoclinic	Triclinic
Formula weight	311.71	359.22
Space group	$P\,21/c$	$P\,\bar{1}$
F(000)	640	334
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
Z	4	2
Absorption coefficient	0.293 mm^{-1}	2.706 mm^{-1}
Calculated density	1.522 Mg/m^3	1.57 Mg/m^3
No. Parameters	199	199
R-obs	0.2190	0.042
wR$_2$ (all)	0.4104	0.126
Theta range for data collection	3.23 to 25.00 °	1.857-26.371°
h min, max; k min, max; l min, max	-9<=h<=9, -30<=k<=28, -9<=l<=8	-10-10,-10-10,-14-14
Max. and min. Transmission	0.9601 and 0.9357	0.6014 and 0.5343
Goof(S)	1.099	0.995
No. Unique reflections.	2388	2106
Temperature	150(2) K	293 K
Largest diff. peak and hole	0.9601 and 0.9357e.A^{-3}	0.37 and 0.74 e.A^{-3}

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Table 2(Ia) Bond lengths [A°]

Atom 1-atom 2	Angle
Cl(1)-C(12)	1.740(10)
O(1)-C(7)	1.347(13)
O(1)-C(8)	1.411(13)
O(2)-C(16)	1.251(13)
O(3)-C(16)	1.371(14)
O(3)-C(15)	1.408(13)
N(1)-C(1)	1.108(14)
C(1)-C(2)	1.467(16)
C(2)-C(3)	1.388(16)
C(2)-C(7)	1.404(16)
C(3)-C(4)	1.371(16)
C(4)-C(5)	1.350(18)
C(5)-C(6)	1.393(17)
C(6)-C(7)	1.381(14)
C(8)-C(9)	1.498(15)
C(9)-C(17)	1.367(15)
C(9)-C(10)	1.411(17)
C(10)-C(15)	1.391(16)
C(10)-C(11)	1.415(15)
C(11)-C(12)	1.368(16)
C(12)-C(13)	1.384(17)
C(13)-C(14)	1.367(16)
C(14)-C(15)	1.372(17)
C(16)-C(17)	1.406(16)

Table 2(Ib) Bond lengths [A°]

Atom 1-atom 2-atom 3	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)
Br(1) - C(14)	1.912(4)
C(5) - C(6)	1.413(6)
C(5) - C(4)	1.384(6)

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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)

Table 2(IIa) Bond angles [°]

Atom1-atom2-atom3	Angle
C(7)-O(1)-C(8)	116.8(8)
C(16)-O(3)-C(15)	121.3(8)
N(1)-C(1)-C(2)	178.1(14)
C(3)-C(2)-C(7)	119.9(10)
C(3)-C(2)-C(1)	120.2(11)
C(7)-C(2)-C(1)	120.0(10)
C(4)-C(3)-C(2)	121.2(12)
C(5)-C(4)-C(3)	118.9(11)
C(4)-C(5)-C(6)	121.6(11)
C(7)-C(6)-C(5)	120.3(12)
O(1)-C(7)-C(6)	125.1(11)
O(1)-C(7)-C(2)	116.8(9)
C(6)-C(7)-C(2)	118.0(11)
O(1)-C(8)-C(9)	112.7(9)
C(17)-C(9)-C(10)	118.1(10)
C(17)-C(9)-C(8)	121.7(11)
C(10)-C(9)-C(8)	120.2(10)
C(15)-C(10)-C(9)	121.1(10)
C(15)-C(10)-C(11)	116.2(11)
C(9)-C(10)-C(11)	122.6(10)
C(12)-C(11)-C(10)	119.5(10)
C(11)-C(12)-C(13)	121.4(10)
C(11)-C(12)-Cl(1)	118.9(9)
C(13)-C(12)-Cl(1)	119.6(10)
C(14)-C(13)-C(12)	120.9(13)
C(13)-C(14)-C(15)	117.1(11)
C(14)-C(15)-C(10)	124.7(10)
C(14)-C(15)-O(3)	116.7(10)
C(10)-C(15)-O(3)	118.6(11)
O(2)-C(16)-O(3)	114.3(10)
O(2)-C(16)-C(17)	127.2(12)
O(3)-C(16)-C(17)	118.5(10)
C(9)-C(17)-C(16)	122.3(11)

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Table 2(IIb) Bond angles [°]

Atom 1-atom 2-atom 3 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 (3 I) Dihedral angles formed by LSQ-planes

Plane 1

Atom	d
C2	0.0063
C3	0.0034
C4	-0.0155
C5	0.0121
C6	-0.0022
C7	0.0023
O1	-0.0025

Plane 2

Atom	d
C10	-0.0280
C11	0.0062
C12	0.0218
C13	-0.0157
C14	0.0004
C16	0.0133

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Plane 1	
Atom	**d**
C1	-0.0091
C2	0.0083
C3	-0.0007
C4	-0.0060
C5	0.0049
C6	0.0025

Plane 2	
Atom	**d**
C5	-0.0175
C6	0.0216
C7	0.0119
C8	0.0209
C9	-0.0133
C10	-0.0236
O2	-0.0488

Plane 3	
Atom	**d**
C11	0.0036
C12	-0.0027
C13	-0.0021
C14	0.0058
C15	-0.0047

Table (3 II) Dihedral angles formed by LSQ-planes

Plane - plane	Angle (°.)
1 2	15.47(3)

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

Table (4 I). Hydrogen bonding geometry

(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°
C8-H8A…O2^{i}	0.990(1)	2.802(7)	3.529(1)	131
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.

equivalent positions:
 (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

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Table (4 II) .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

Equivalent positions:

(i) -x+2,-y,-z+2

(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°
N1—H1A⋯N2^i	0.86(0)	2.13(2)	2.971 (5)	165
N3—H3A⋯N4^{ii}	0.86(0)	2.19(2)	3.014 (5)	162
N3—H3B⋯O1^{iii}	0.86(0)	2.31(1)	3.086 (5)	150

Symmetry codes: (i) $-x+1, -y, -z+1$ (ii) $-x+1, -y+2, -z$, (iii) $-x+2, -y+1, -z+1$
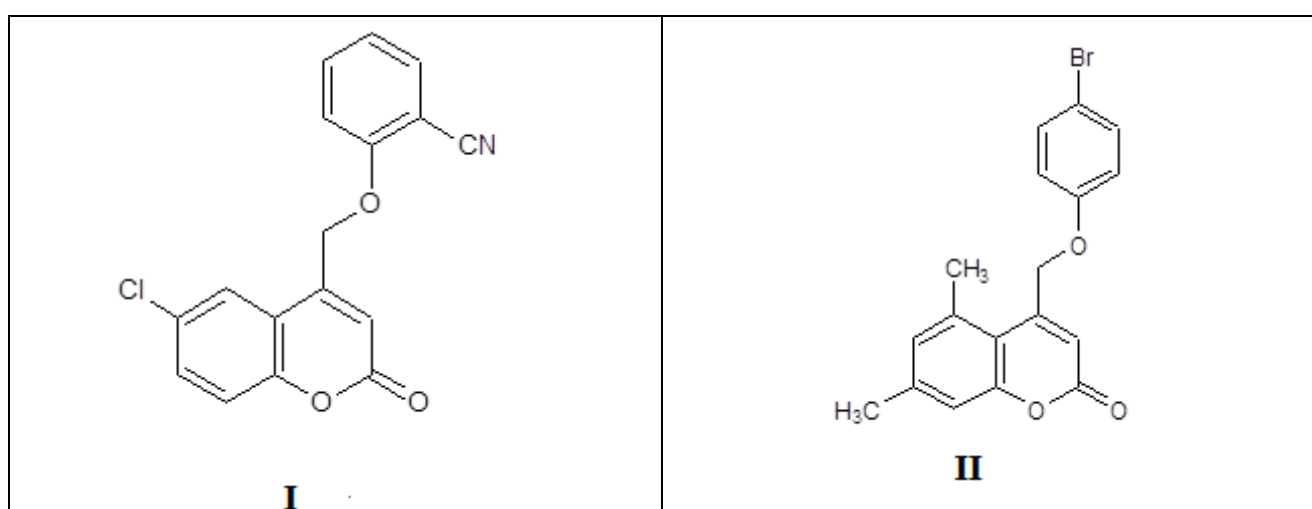
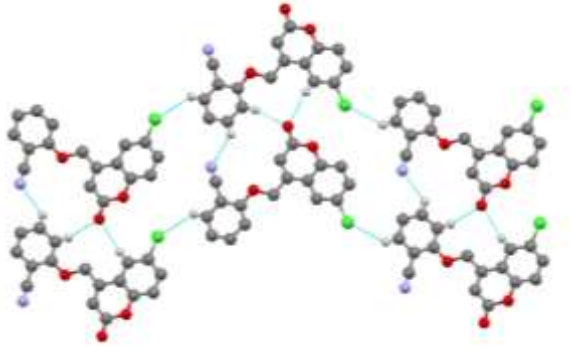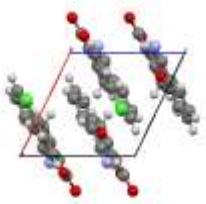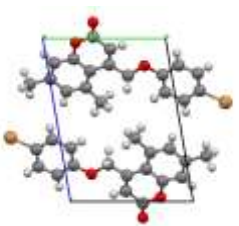

Fig 1. Scheme of title compound I and II
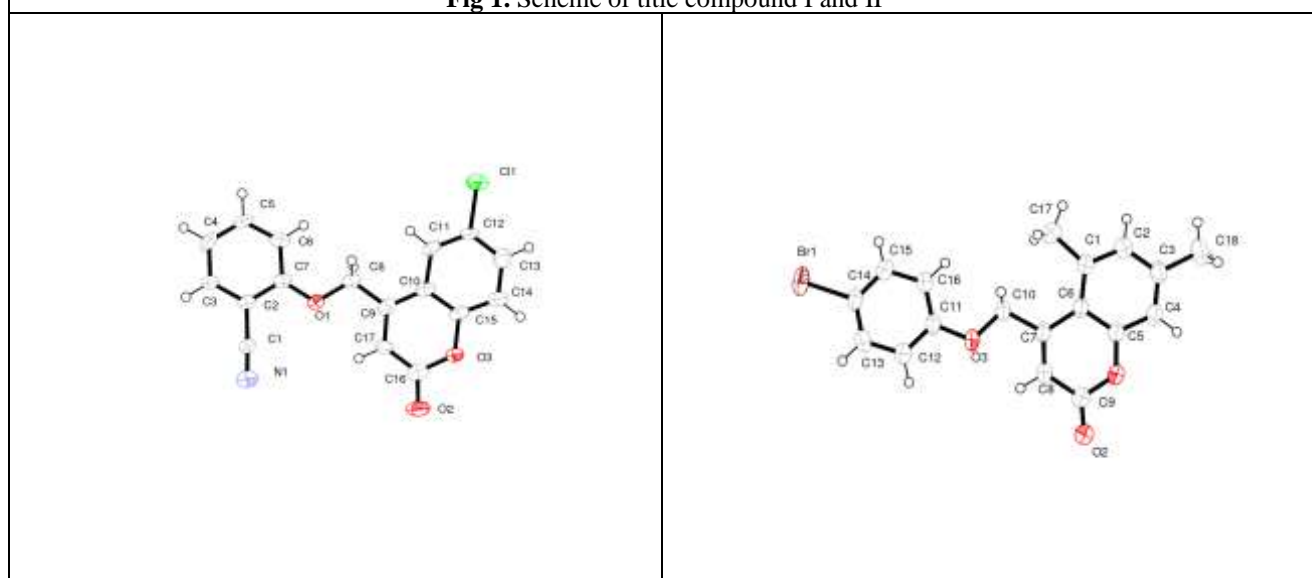
Fig 2. ORTEP diagram of the title molecule with 50% probability displacement ellipsoids with-H atoms of I and II

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Comparative Study of the Crystal Structures of Crystal Structure of 2- [6-Chloro-2-Oxo-2h-Chromen -4-Ylmethoxy]-Benzonitrile. ($C_{17}H_{10}Cl\,N\,O_3$). and 4-(4-Bromo-Phenoxymethyl)-5, 7-Dimethyl-Chromen-2-One ($C_{18}H_{15}Br\,O_3$)

Section A-Research Paper

Fig 3. I Packing of the molecules showing C-H…O hydrogen bonding.

Fig 3. II Packing of the molecules showing C-H…O and Br…Br bonding.

Fig 4 .I Packing diagram viewed down b-axis and molecules oriented as parallel layers along c-axis.

Fig 4. II Packing diagram viewed down b-axis.

Conformation of molecule

The molecule 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.

Molecular Packing

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 along b-axis shown in Fig 4.2.3 further linked by C-

H…Cl (Fig 4.3.3) hydrogen bonds listed in Table 4.2.6(c).

Conformation of molecule

The entire molecular is planar the phenoxy moiety is anti periplanar with respect to the coumarin as indicated by the C10-O5-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 bond angles

There is a significance deviation in bond angle at O1-C5-C4 (114.2(4) °) due to the electronic repulsion of oxygen (O2) atom which is present at C9 carbon atom. 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 releasing methyl group on C18 carbon atom which makes repulsion of electrons.

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Comparative Study of the Crystal Structures of Crystal Structure of 2- [6-Chloro-2-Oxo-2h-Chromen -4-Ylmethoxy]-Benzonitrile. (C₁₇ H₁₀ Cl N O₃), and 4-(4-Bromo-Phenoxymethyl)-5, 7-Dimethyl-Chromen-2-One (C₁₈ H₁₅ Br O₃)

Section A-Research Paper

Molecular Packing

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 4.3.2. The molecule indicates Br…Br interactions (Br1-Br1=3.594Å). The molecule is stabilised by intermolecular C-H…O (Fig 4.3.2) hydrogen bonds listed in Table 4.3.6(c).

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