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Synthesis, Spectral Study and Crystal Structure Analysis of Two Coumarin Derivatives

N. Latha Rani[1], Shivaprasad Shetty[2], N.V. Anil Kumar[3] and M.A. Sridhar[1*]

1. Department of Studies in Physics, Manasagangotri, University of Mysore 570 006, Mysuru, **INDIA**
2. Department of Chemistry, NMAM, Institute of Technology, Nitte, Karkala, Udupi, Karnataka, **INDIA**
3. Department of Chemistry, Manipal Institute of Technology, Manipal, Udupi, Karnataka, **INDIA**

Email: mas@physics.uni-mysore.ac.in

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ABSTRACT

In this paper we will discuss the crystal structure of two coumarin molecules Ethyl 2-(4-methyl-2-oxo-chromen-7-yl) oxyacetate (c4), 2-(4-Methyl-2-oxo-chromen-7-yl) oxyacetohydrazide (c5). The compound c4 crystallizes in the monoclinic crystal system with the space group $P2_1/n$. The unit cell parameters are a = 12.502(3) Å, b = 8.324(2) Å, c = 13.477(3) Å, β = 115.558(15), Z = 4. The compound c5 crystallizes in the monoclinic crystal system with the space group $P2_1/c$. The unit cell parameters are a = 10.0839(7) Å, b = 14.5972(12) Å, c = 8.4573(6) Å, β = 112.489(4), Z = 4.

Highlights

- Synthesis of two coumarin derivatives Ethyl 2-(4-methyl-2-oxo-chromen-7-yl) oxyacetate and 2-(4-Methyl-2-oxo-chromen-7-yl) oxyacetohydrazide has been discussed in this manuscript.
- The two coumarin derivatives were characterized by FTIR, ^{1}H NMR and single crystal X-ray diffraction.
- This manuscript highlights the details of structural study of two coumarin molecules.
- The two molecules crystallize in monoclinic crystal system.
- The molecular arrangement in the first compound shows that the formation of $R_2^2(22)$ through C-H...O hydrogen bonds.
- The second compound shows the formation of $R_2^2(6)$ inverted dimer through N-H...N hydrogen bonds and $R_2^2(12)$ inverted dimer through N-H...O hydrogen bonds.

Keywords: Coumarin, phytochemical, Graph-set theory, intermolecular interactions, intramolecular.

INTRODUCTION

Coumarin (2-oxo-2H-chromene) belongs to the benzopyrone class. Benzopyrones are classified into two groups benzo-*α*-pyrones and benzo-*γ*-pyrones. Coumarins belong to benzo-*α*-pyrones class. The basic structure of the coumarin consists of a benzene ring fused to a pyrone nucleus. Coumarins are a distinct class of oxygen substituted heterocycles, which are widely distributed in nature.

As one of the old class of compounds coumarin has got ample pharmacological properties. Coumarin and their derivatives may serve as important compounds in the development of anti-microbial therapy [1]. They are a promising heterocyclic compound exhibiting anti-viral, anti-diabetic, anti-oxidant, anti-parasitic, anti-helmintic, anti-proliferative, anti-convulsant, anti-infl amatory, and anti-hypertensive activities [2], anti-coagulant, anti-cancer, antiviral, anti-malarial etc [3].
Investigations show that the coumarin derivatives with halogen substituents have best mi-crobiological activity [4]. Chlorine substituted 4-hydroxycoumarin derivative has potent anti-coagulant activity [5]. It has been reported that the 7-hydroxycoumarin shows potent anti-tumour activity [6]. Simple coumarins can also be used to treat cancer, and also the side effects caused by radiotherapy [7]. A few of the polyesters derived from 6-(N-(3-Chlorophenyl) piperazinyl)-2,4-bis- (7-hydroxycoumarin-4-acetyl chloride)-1,3,5-triazine may be useful for applications in automobile and marine engineering [8].

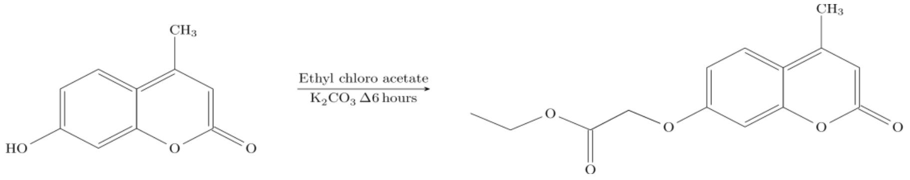
Owing to the importance of coumarin nucleus, herein we discuss the structure of two coumarin derivatives.

MATERIALS AND METHODS

The compounds c4 and c5 were purchased from Sigma-Aldrich. Compound c4 was re-crystallized using ethanol as a solvent, while DMSO was used for the compound c5.

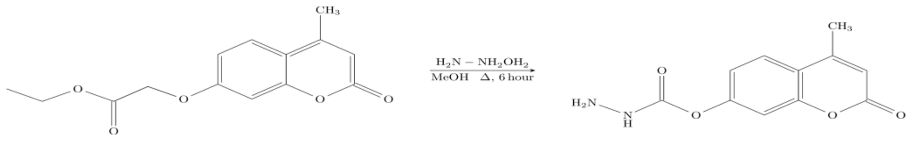
Synthesis of Compounds c4 and c5

Compound c4: 7-hydroxy-4-methyl-coumarin (0.0454mol) and ethyl chloroacetate (0.0454mol) was taken in a round bottomed flask and was dissolved in 40 mL acetone. To the mixture, K_2CO_3 (equimolar) was added. The mixture was refluxed for 24 h. The reaction was monitored using thin layer chromatography (mobile phase: 6 mL of hexane and 4 mL of ethyl acetate). After completion of the reaction, solution was poured to ice-cold water and precipitate was filtered and dried. Melting point (88˚C to 90˚C) of the dried product was noted. Schematic diagram of compound c4 is shown in the scheme-1.



Scheme 1: Schematic diagram of compound c4

Compound c5: The starting material ethyl 2-(4-methyl-2-oxo-chromen-7-yl) oxyacetate (0.038mol) and hydrazine hydrate (0.038mol) taken in round bottomed flask and was dissolved in 50 mL of methanol. The mixture was refluxed for 3 h. The reaction was monitored using thin layer chromatography (mobile phase: 6 mL of hexane and 4 mL of ethyl acetate). After completion of the reaction, solution was transferred to crushed ice and precipitated. The precipitate was filtered and dried. Melting point (192˚C to 196˚C) of the dried product was noted. Schematic diagram of compound c5 is shown in the scheme-2.



Scheme 2: Schematic diagram of compound c5

Crystal Structure Determination: A suitable single crystals of approximate dimensions 0.23 × 0.22 × 0.21 mm was carefully chosen for intensity data collection. X-ray intensity data were collected on a Bruker

X8 Proteum X-ray diffractometer equipped with CuK_α radiation of wavelength λ = 1.54178 Å. Data were collected at 293 K. Data were corrected for Lorentz, polarization and absorption factors.

The crystal structures were solved by direct methods using *SHELXS* [9]. An *E*-map drawn with the correct set of phases revealed all the non-hydrogen atoms of the molecules. The crystal structures were refined by full-matrix least squares refinement against F^2 using *SHELXL*-97 [10]. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at chemically acceptable positions. The final refinement cycle converged with $R = 0.0511$ and $wR_2 = 0.1608$. Goodness of fit on F^2 is 1.03 for the compound c4. The final refinement cycle converged with $R = 0.0668$ and $wR_2 = 0{:}1992$. Goodness of fit on F^2 is 1.079 for the compound c5.

RESULTS AND DISCUSSION

FT-IR Spectral Analysis: c4 in FT-IR spectra, the peaks observed at 1704.96 cm^{-1} are assigned to C=O. The peaks at 1072.35 cm^{-1} and 1604.66 cm^{-1} are due to C-O-C and C=O stretching vibrations respectively. c5 in FT-IR spectra, the peaks observed at 3263.3 cm^{-1} are assigned to N-H. The peaks at 1674.1 cm^{-1} and 1604.63 cm^{-1} are due to C-O-C and C=O stretching vibrations respectively.

^{1}H NMR Spectral analysis: c4: δ = 7.69 (1H, d, J = 9.5 Hz, 6-H), 6.99 (2H, m, 5, 8-H), 6.23 (1H, s, 3-H), 4.93 (2H, s, OCH_2), 4.18 (2H, q, J = 7.0 Hz, CH_2), 2.39 (3H, s, CH_3), 1.22 (3H, t, J = 7.0 Hz, CH_3).c5:δ = 9.41 (1H, s, NH), 7.69 (1H, d, J = 8.8 Hz, 6-H), 7.00 (1H, dd, J = 8.8 Hz, J = 2.4 Hz, 5-H), 6.9 (1H, d, J = 10.3 Hz, 8-H), 6.21 (1H, s, 3-H), 4.61 (2H, s, NH_2), 4.35 (2H, s, OCH_2), 2.39 (3H, s, CH_3).

Description of the Crystal Structures: The bond lengths and angles of the compounds c4 and c5 are in fairly good agreement with the standard values [11] and with those of other reported coumarin derivatives. The geometrical calculations were carried out using *PLATON* [12,13] on GNU/Linux platform. The thermal ellipsoid plot and the molecular packing diagrams were generated using mercury [14,15]. The crystal data and structure refinement details of the compounds c4 and c5 are given in table 1. Thermal ellipsoid plot of compound c4 is shown in the Figure 1.

Table 1. Crystal data and structure refinement details

	c4	c5
CCDC deposit number	1059541	1446978
Empirical formula	$C_{14}H_{14}O_5$	$C_{12}H_{12}N_2O_4$
Formula weight	262.25	248.24
Temperature	293 K	296 K
Wavelength	1.54178 Å	1.54178 Å
Reflns. for unit cell determination	1963	1856
θ range for cell determination	4.00° to 64.30°	4.70° to 64.50°
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a = 12.502(3) Å, b = 8.324(2) Å, c = 13.477(3) Å, β = 115.558(15)°	a = 10.0839(7) Å, b = 14.5972(12) Å, c = 8.4573(6) Å, β = 112.489(4)°
Volume	1265.3(5) Å^3	1150.22(15) Å^3
Z	4	4

Density(calculated)	1.377 Mg m^{-3}	1.433 Mg m^{-3}
Absorption coefficient	0.881 mm^{-1}	0.921 mm^{-1}
F_{000}	552	520
Crystal size	0.23 × 0.22 × 0.21 mm	0.18 × 0.19 × 0.20 mm
θ range for data collection	4.04° to 64.34°	4.75° to 64.45°
Index ranges	$-14 \leq h \leq 14$ $-7 \leq k \leq 9$ $-15 \leq l \leq 14$	$-11 \leq h \leq 11$ $-14 \leq k \leq 16$ $-9 \leq l \leq 9$
Reflections collected	4073	5353
Independent reflections	1963 [R_{int} = 0.037]	1856 [R_{int} = 0.045]
Data / restraints / parameters	1963 / 0 / 174	1856 / 0 / 164
Goodness-of-fit on F^2	1.034	1.079
Final [$I > 2\sigma(I)$]	$R1$ = 0.0511, $wR2$ = 0.1518	$R1$ = 0.0668, $wR2$ = 0.1992
Largest diff. peak and hole	0.222 and −0.181 eÅ^{-3}	0.561 and −0.455 eÅ^{-3}

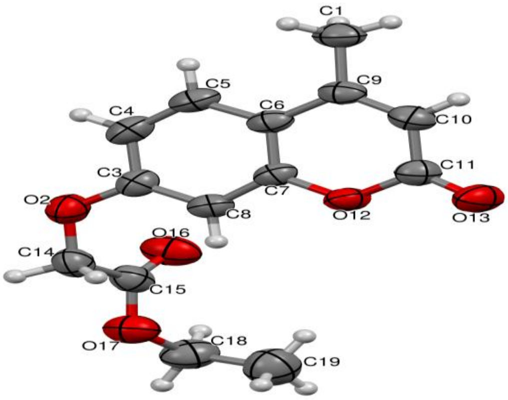


Figure 1. Thermal ellipsoid plot drawn at 50% probability of c4.

c4: The six C–C bond lengths lie in the range 1.345(3) Å to 1.448(3) Å for the pyrone ring (ring I: O12-C7-C6-C9-C10-C11) and 1.364(3) Å to 1.400(3) Å for the phenyl ring (ring II: C3-C4-C5-C6-C7-C8). The bond angles lie in the range of 116.9(2)° to 122.8(2)° for ring I; similarly for ring II the range is 116.2(2)° to 123.6(2)°. The average of these values is ≈ 120°. This confirms that the rings are in trigonal hybridization or sp^2 hybridization. The bond length between the atoms C9 and C10 is 1.345(3) Å. This confirms the localized double bond nature.

The pyrone ring is planar (r.m.s. deviation is 0.007(2) Å) with a maximum deviation of 0.009(1) Å observed for the atom O12. The phenyl ring is planar (r.m.s. deviation is 0.003(2) Å) with a maximum deviation of 0.004(2) Å observed for the atom C5. The 10-membered ring, 2H-chromene is also planar (r.m.s. deviation is 0.013(2) Å) with a maximum deviation of 0.018(2) Å observed for the atom C11. The dihedral angles between the pyrone and the phenyl rings are -0.1(3)° (for C5-C6-C7-C8) and 0.2(3)° (for C9-C6-C7-O12). This explains the perfect planarity of the coumarin moiety.

The bond angle between the atoms O12-C11-O13 is (116.1(2)°) is smaller than the bond angle between the atoms O13-C11-C10 (127.0(2)°). This is due to the steric effects. Generally, in coumarin derivatives the bond angle at one of the junctions of the 2H-chromene will be smaller than 120° and the other will be greater than 120°. This can be verified by the bond angles 115.7(2)° and 125.0(2)° observed for the atoms

O12-C7-C8 and C5-C6-C9 respectively. These angles are found at the junctions of the pyrone ring (ring I) and the phenyl ring (ring II) of the 2H-chromene.

The rings I and II are in *syn-periplanar* (+*sp*) conformation. The bond angle for the atoms O13-C11-C10 is 127.0(2)°, which is slightly larger than the standard value. This is attributed to the lone-pair interactions between the atoms O12 and O13. Selected bond lengths, angles and torsion angles for non-hydrogen atoms of compound c4 are given in Tables 2 and 3 respectively. The molecular structure is stabilized by the weak inter and intramolecular interactions of the type C-H…O. The molecules exhibit strong π-π stacking, which shows short centroid-centroid distances (see table 5). The π-π interactions take place between pyrone and the phenyl rings of the adjacent molecules. In the crystal packing C-H…O intermolecular hydrogen bonds link pairs of molecules to form inversion dimers forming $R_2^2(22)$ graph-set motif [16]. Packing of the molecules along with the unit cell when viewed down the *a*-axis is as shown in Figure 2. Details of the hydrogen bonds are given in the Table 4. Figure 3 shows the dimer with the inversion center.

Table 2. Bond lengths and angles for non-hydrogen atoms of compound c4

Atoms	**Length (Å)**	**Atoms**	**Angle (°)**
O2-C3	1.371(3)	C3-O2-C14	118.9(2)
O2-C14	1.411(3)	C7-O12-C11	122.0(2)
O12-C7	1.372(2)	C15-O17-C18	118.8(2)
O12-C11	1.388(3)	O2-C3-C4	115.2(2)
O13-C11	1.207(3)	O2-C3-C8	124.6(2)
O16-C15	1.196(3)	C5-C6-C7	116.2(2)
O17-C15	1.322(3)	C5-C6-C9	125.0(2)
C3-C8	1.382(3)	C7-C6-C9	118.8(2)
C4-C5	1.364(3)	O12-C7-C6	120.7(2)
C5-C6	1.400(3)	C6-C7-C8	123.6(2)

Table 3: Torsion angles for non-hydrogen atoms of compound c4

Atoms	**Angle (°)**	**Atoms**	**Angle (°)**
C14-O2-C3-C4	174.3(2)	C5-C6-C9-C1	-0.3(3)
C14-O2-C3-C8	-6.6(3)	C5-C6-C9-C10	-178.8(2)
C11-O12-C7-C8	178.4(2)	C9-C6-C7-C8	-179.5(2)
C7-O12-C11-C10	1.7(3)	C7-C6-C9-C10	0.5(3)
C11-O12-C7-C6	1.3(3)	C9-C6-C7-O12	0.2(3)
C7-O12-C11-O13	-178.8(2)	C7-C6-C9-C1	179.0(2)
C18-O17-C15-C14	-174.5(2)	C5-C6-C7-C8	-0.1(3)
C3-C4-C5-C6	0.6(4)	O2-C14-C15-O16	0.3(4)
C4-C5-C6-C7	-0.5(3)	O2-C14-C15-O17	-178.6(2)
C4-C5-C6-C9	178.9(2)		

Table 4. Hydrogen-bond geometry of compound c4

D-H...A	D−H (Å)	H...A (Å)	D...A (Å)	D-H...A (º)
C14-H14A...O16[a]	0.97	2.59	3.498(3)	156
C14-H14B...O13[b]	0.97	2.54	3.446(3)	156
C18-H18A...O16[c]	0.97	2.39	2.730(3)	100
C18-H18B...O13[d]	0.97	2.54	3.457(3)	158

a: 3/2 − x, 1/2 + y, 3/2 − z
c: intramolecular interaction
b: 1/2 − x, 1/2 + y, 3/2 − z
d: 1/2 + x, 1/2 − y, −1/2 + z

Table 5. Geometry of π-π interactions of compound c4

CgI	CgJ	d_1(Å)	α (º)	β (º)	γ (º)	d_2(Å)	d_3(Å)	d_4(Å)
Cg1	Cg1[a]	3.682(2)	0	20.2	20.2	−3.455(8)	−3.455(8)	1.273
Cg1	Cg2[a]	3.857(2)	1.16(1)	27.2	26.3	−3.458(8)	−3.429(9)	--
Cg2	Cg1[a]	3.857(2)	1.16(1)	26.3	27.2	−3.429(9)	−3.458(8)	--
Cg2	Cg2[b]	3.639(2)	0	14.4	14.4	3.525(8)	3.525(9)	0.905

a: 1 − x, −y, 2 − z
b: 1 − x, 1 − y, 2 − z

Cg1 is the centre of gravity of the pyrone ring (O12-C7-C6-C9-C10-C11); Cg2 is the centre of gravity of the phenyl ring (C3-C4-C5-C6-C7-C8); d_1 is d[CgI...CgJ] represents the centroid-centroid distance between the rings; α represents the dihedral angle between the ring planes; β represents the angle between the centroid vector CgI...CgJ and the normal to the plane I; γ represents the angle between the centroid vector CgI...CgJ and the normal to the plane J; d_2 is d[CgI...P] represents the perpendicular distance of CgI on the ring plane J; d_3 is d[CgJ...P] represents the perpendicular distance of CgJ on the ring plane I; d_4 is d[a] represents the vertical displacement between the ring centroids.

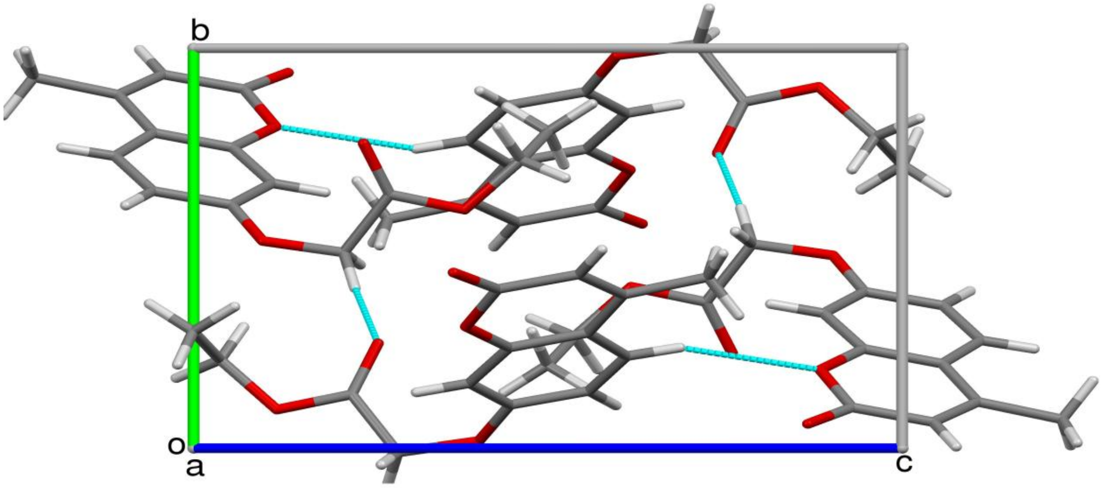


Figure 2. Packing of molecules down a-axis of compound c4

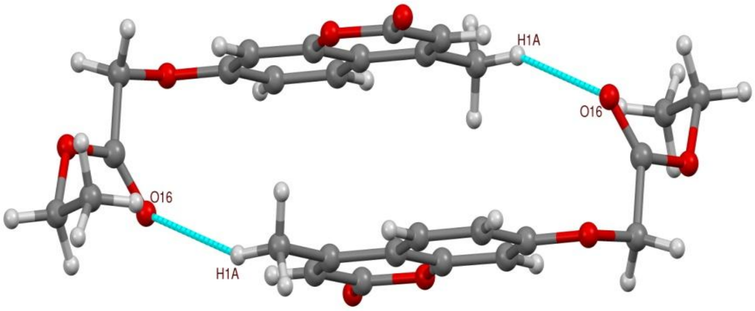


Figure 3. Molecules showing the formation of R_2^2 (22) through C-H...O hydrogen bonds (dashed lines) of compound c4

c5: Thermal ellipsoid plot of c5 is shown in the figure 4. The six C-C bond lengths lie in the range 1.346(3) Å to 1.447(3) Å for the pyrone ring (ring I: O12-C7-C6-C9-C10-C11) and 1.363(4) Å to 1.406(3) Å for the phenyl ring (ring II: C3-C4-C5-C6-C7-C8). The bond angles lie in the range of 116.9(2)º to 122.8(2)º for ring I; similarly for ring II the range is 116.8(2)º to 122.7(2)º. The average of these values is ≈ 120º. This confirms that the rings are in trigonal hybridization or *sp*2 hybridization. The bond length between the atoms C9 and C10 is 1.346(3) Å. This confirms the localized double bond nature. The pyrone ring is planar (r.m.s. deviation is 0.009(2) Å) with a maximum deviation of 0.009(2) Å observed for the atom O12. The phenyl ring is planar (r.m.s. deviation is 0.002(2) Å) with a maximum deviation of 0.003(2) Å observed for the atom C5. The 10-membered ring, 2H-chromene is also planar (r.m.s. deviation is 0.009(2) Å) with a maximum deviation of 0.015(2) Å observed for the atom C11. The dihedral angles between the pyrone and the phenyl rings are 0.3(3)º (for C5-C6-C7-C8) and 0.2(3)º (for C9-C6-C7-O12). This explains the perfect planarity of the coumarin moiety.

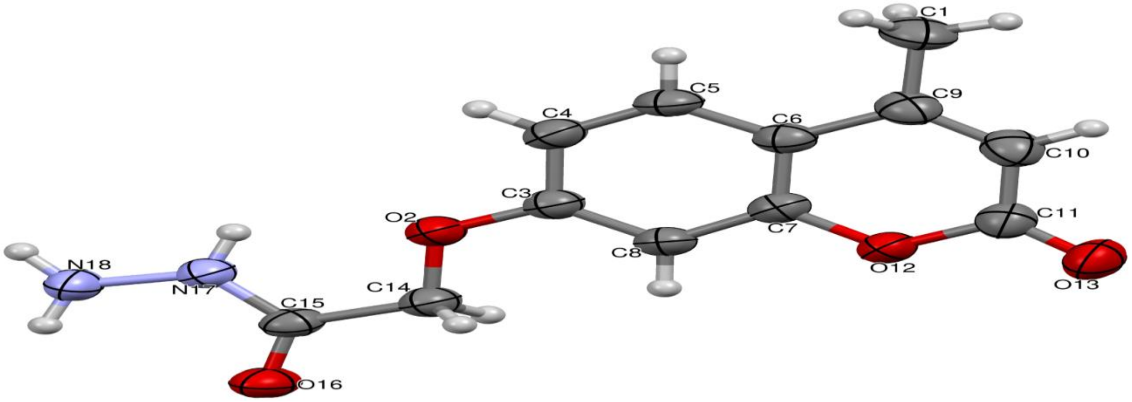


Figure 4. Thermal ellipsoid plot drawn at 50% probability of c5

The bond angle between the atoms O12-C11-O13 is (116.4(2)º) is smaller than the bond angle between the atoms O13-C11-C10 (126.8(2)º). This is due to the steric effects. Generally, in coumarin derivatives the bond angle at one of the junctions of the 2H-chromene will be smaller than 120º and the other will be greater than 120º. This can be verified by the bond angles 115.7(2)º and 124.8(2)º observed for the atoms O12-C7-C8 and C5-C6-C9 respectively. These angles are found at the junctions of the pyrone ring (ring I) and the phenyl ring (ring II) of the 2H-chromene.

The rings I and II are in *syn-periplanar* (+*sp*) conformation. The bond angle for the atoms O13-C11-C10 is 126.8(2)º, which is slightly larger than the standard value. This is attributed to the lone-pair interactions between the atoms O12 and O13.The bond lengths, angles and torsion angles for non-hydrogen atoms of compound c5 are given in tables 6 and 7 respectively.

Table 6. Bond lengths and angles for non-hydrogen atoms of compound c5.

Atoms	Length (Å)	Atoms	Angle (°)
O2-C3	1.366(3)	C3-O2-C14	117.6(2)
O2-C14	1.422(3)	C7-O12-C11	121.4(2)
O12-C7	1.377(2)	N18-N17-C15	122.7(2)
O12-C11	1.384(3)	O2-C3-C4	115.1(2)
O13-C11	1.204(3)	C4-C3-C8	121.0(2)
O16-C15	1.230(2)	O2-C3-C8	124.0(2)
N17-N18	1.410(3)	C3-C4-C5	119.2(2)
N17-C15	1.330(3)	C4-C5-C6	122.1(2)
C1-C9	1.501(4)	C5-C6-C9	124.8(2)
C3-C4	1.406(3)	C7-C6-C9	118.4(2)
C3-C8	1.377(3)	C5-C6-C7	116.8(2)
C4-C5	1.363(4)	O12-C7-C6	121.6(2)
C5-C6	1.406(3)	O12-C7-C8	115.7(2)

Table 7. Torsion angles for non-hydrogen atoms of compound c5

Atoms	Angle (°)	Atoms	Angle (°)
C14-O2-C3-C4	177.4(2)	C5-C6-C9-C1	-0.3(4)
C14-O2-C3-C8	-2.5(3)	C5-C6-C7-O12	-179.6(2)
C3-O2-C14-C15	176.5(2)	C5-C6-C9-C10	178.6(2)
C11-O12-C7-C8	-178.6(2)	C9-C6-C7-O12	0.2(3)
C7-O12-C11-C10	-1.6(3)	C9-C6-C7-C8	-180.0(2)
C11-O12-C7-C6	1.2(3)	C7-C6-C9-C10	-1.2(3)
C7-O12-C11-O13	179.2(2)	C5-C6-C7-C8	0.3(3)
N18-N17-C15-C14	180.0(2)	C7-C6-C9-C1	180.0(2)
N18-N17-C15-O16	1.1(3)	C6-C7-C8-C3	0.1(3)
C4-C3-C8-C7	-0.2(3)	O12-C7-C8-C3	180.0(2)
O2-C3-C8-C7	179.7(2)	C6-C9-C10-C11	0.7(4)
C8-C3-C4-C5	0.0(4)	C1-C9-C10-C11	179.6(2)
O2-C3-C4-C5	-180.0(2)	C9-C10-C11-O13	179.7(3)
C3-C4-C5-C6	0.4(4)	C9-C10-C11-O12	0.6(4)
C4-C5-C6-C7	-0.5(3)	O2-C14-C15-N17	7.4(3)
C4-C5-C6-C9	179.7(2)	O2-C14-C15-O16	-173.7(2)

The supramolecular architecture of the molecules in two-dimensional arrangement can be viewed in the packing diagrams. This involves one N-H...O intramolecular hydrogen bond, two N-H...N and a C-H...O intermolecular hydrogen bonds. The packing indicates that the molecular structure is further reinforced by π-π interactions between pyrone and the phenyl rings of the adjacent molecules. The molecular packing diagram viewed along *c*-axis shows that the molecules are packed together to form a zig zag pattern. Packing of the molecules along with the unit cell when viewed down the *a* and *c*-axes are as shown in Figures 5 and 6 respectively.

The atom N18 acts as an acceptor via the atom H17 to nitrogen N17 in the molecule at 2-x, 1-y, -1-z, thus forming a strong N-H...N hydrogen bond. These intermolecular interactions take place in pairs, thus forming inverted dimers with $R_2^2(6)$ graph-set motif. The molecular structure also shows N-H...O hydrogen bonding with the adjacent molecules forming inverted dimers with $R_2^2(12)$ graph-set motif. In addition to this, the molecular structure also exhibits a pair of C-H...O intermolecular hydrogen bond interactions linking the molecules into dimer arrangement forming $R_2^2(8)$ graph-set motif [16].

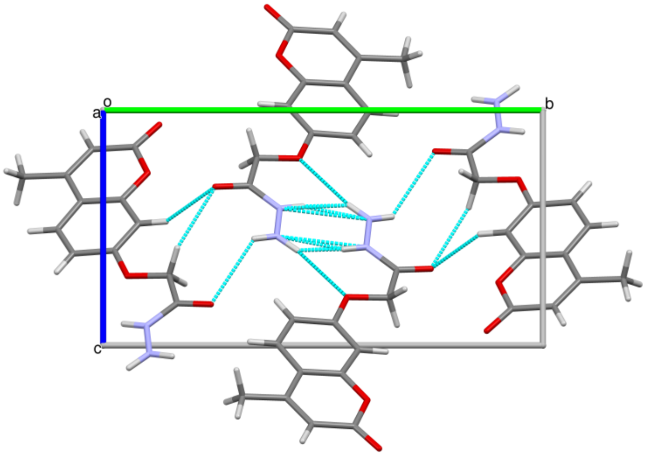


Figure 5. Packing of molecules down a-axis of compound c5

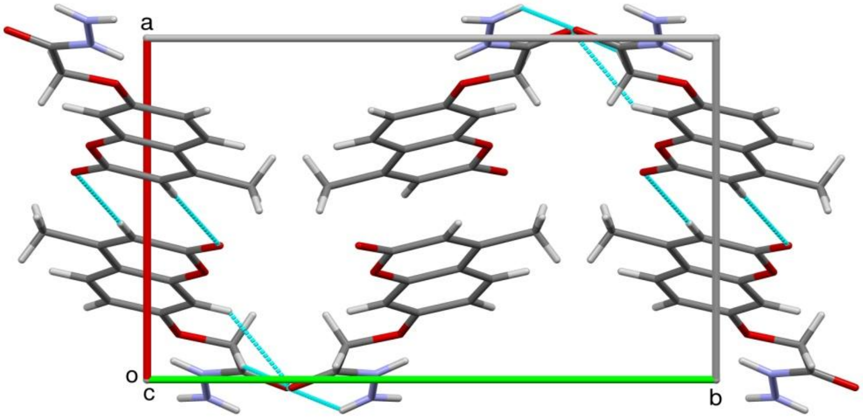


Figure 6. Packing of molecules down c-axis of compound c5

Details of the hydrogen bonds and π-π stacking interactions are given in the Tables 8 and 9 respectively.

Table 8: Hydrogen-bond geometry of compound c5

D-H...A	D−H (Å)	H...A (Å)	D...A (Å)	D-H...A (º)
N17-H17...O2[a]	0.86	2.16	2.580(3)	110
N17-H17...N18[b]	0.86	2.28	3.004(3)	143
N18-H18B...N17[b]	0.86	2.34	3.004(3)	135
C14-H14A...O16[c]	0.97	2.42	3.324(3)	156

a: intramolecular interaction *b*: 2 − x, 1 − y, −1 – z, *c*: x, 3/2 − y, 1/2 + z

Table 9. Geometry of π-π interactions of compound c5

CgI	CgJ	d_1(Å)	*α* (º)	*β* (º)	*γ* (º)	d_2(Å)	d_3(Å)	d_4(Å)
Cg1	Cg1[a]	3.874(1)	0.00(1)	27.6	27.6	−3.432(9)	−3.432(9)	1.797
Cg1	Cg2[a]	3.642(1)	0.66(1)	18.7	19.0	−3.444(9)	−3.445(9)	--
Cg2	Cg1[a]	3.642(1)	0.66(1)	19.0	18.7	−3.450(9)	−3.444(9)	--

a: 1 − x, 1 − y, −z Cg1 is the center of gravity of the pyrone ring (O12-C7-C6-C9-C10-C11); Cg2 is the center of gravity of the phenyl ring (C3-C4-C5-C6-C7-C8); d_1 is *d*[CgI...CgJ] represents the centroid-centroid distance between the rings; *α* represents the dihedral angle between the ring planes; *β* represents the angle between the centroid vector CgI...CgJ and the normal to the plane I; *γ* represents the angle between the centroid vector CgI...CgJ and the normal to the plane J; d_2 is *d*[CgI...P] represents the perpendicular distance of CgI on the ring plane J; d_3 is *d*[CgJ · · · P] represents the perpendicular distance of CgJ on the ring plane I; d_4 is *d*[a] represents the vertical displacement between the ring centroids.

The molecular plots showing the formation of inverted dimers through N-H...N and N-H...O hydrogen bonds (dashed lines) and dimer through C-H...O hydrogen bond are shown in Figures 7, 8, 9 respectively.

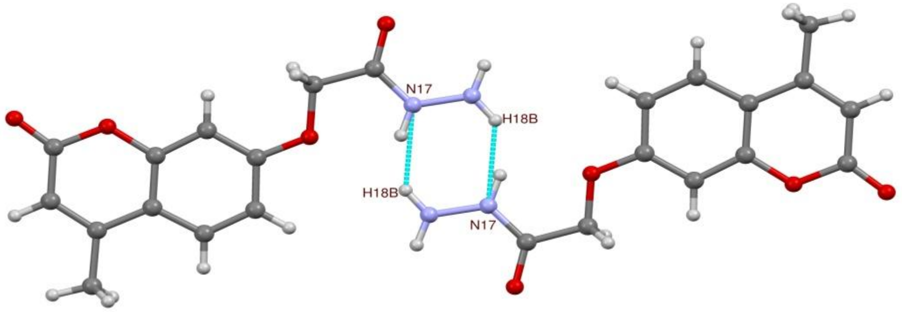


Figure 7. Molecules showing the formation of $R_2^2(6)$ inverted dimer through N-H...N hydrogen bonds (dashed lines) of compound c5

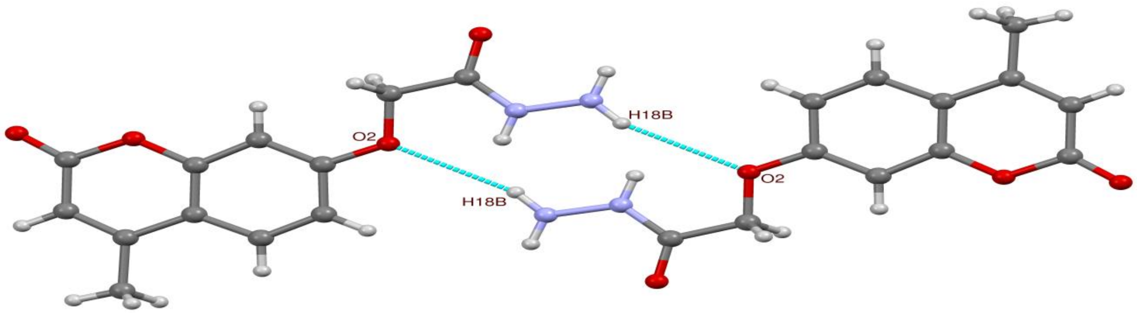


Figure 8. Molecules showing the formation of R_2^2 (12) inverted dimer through N-H...O hydrogen bonds (dashed lines) of compound c5

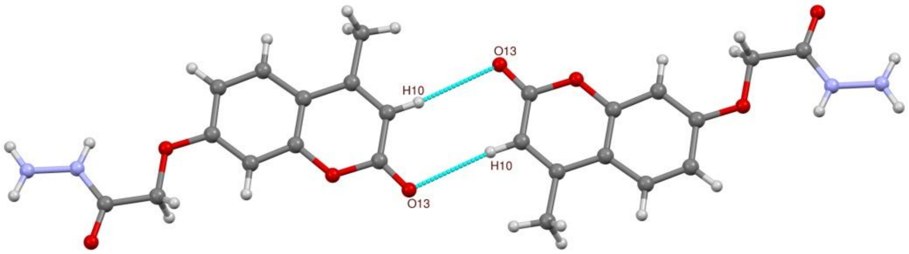


Figure 9. Molecules showing the formation of $R_2^2(8)$ dimer through C-H...O hydrogen bonds (dashed lines) of compound c5

APPLICATIONS

Coumarin has got ample pharmacological properties. The current work deals with structures of two coumarin molecules. This research work is a helpful addition to the library of drug molecules — whenever there is a need for a compound with these properties, one can then lookup for the same in this library.

CONCLUSIONS

The compounds c4 and c5 crystallizes in monoclinic crystal system with space groups $P2_1/n$, $P2_1/c$ respectively. The compounds are stabilized by C-H...O type intermolecular interactions. The compound c5 also exhibits N-H...N type intermolecular interactions. The compounds exhibit π-π interactions. The compound c4 exhibit C-H...O type intra-molecular interactions while the compound c5 exhibits N-H...O type intramolecular interactions.

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AUTHORS' ADDRESSES

1. **N. Latha Rani**
Research Scholar, Department of Studies in Physics, Manasagangotri,
University of Mysore 570 006, Mysuru, Karnataka, India
Email:latharani@uomphysics.net
2. **M. Shivaprasad Shetty**
Assistant Professor, Department of Chemistry, NMAM, Institute of Technology,
Nitte, Karkala, Udupi, Karnataka, India
Email: shivaprasad@nitte.edu.in
3. **N.V. Anil Kumar**
Associate Professor, Manipal Institute of Technology,
Manipal, Udupi, Karnataka, India
Email:nv.anil@manipal.edu
4. **M.A. Sridhar**
Professor, Department of Studies in Physics, Manasagangotri,
University of Mysore 570 006, Mysuru, Karnataka, India
Email: mas@physics.uni-mysore.ac.in