COMPARATIVE STUDY OF THE CRYSTAL STRUCTURES OF 6-CHOLORO 4-[(4-METHYL) PHENOXY METHYL] COUMARIN ($C_{17} H_{13} CL O_3$) AND 4-[5-CHLORO-3-(4-CHLORO-PHENYL) BENZOFURAN -2-YL]-6 METHYL-CHROMEN -2-ONE ($C_{24} H_{14} CL_2 O_3$).

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ABSTRACT

4-Phenoxymethylcoumarin was reported by Balasubramanian et al 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, 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 using chloro/bromo substituents have been subjected to X-ray diffraction studies.

Keywords: Aryloxymethylcoumarins, benzofuran, crystal x-ray study, Molecular Packing and hydrogen bonding.

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INTRODUCTION

Compounds have been used for the synthesis of a variety of ethers, amines, sulphides; which have been screened for anti-microbials, anti-inflammatory and analgesic activities aryloxymethylcoumarins were screened for their anti-microbial agents and due to the biochemical importance of 7-methoxy-4-bromomethylcoumarin. In view of this, it was thought of considerable interest and to compare two Crystal structures of 6-Choloro 4-[(4-methyl) phenoxy methyl] coumarin ($C_{17} H_{13} Cl O_3$) and 4-[5-Chloro-3-(4-chloro-phenyl) benzofuran -2-yl]-6 methyl-chromen -2-one ($C_{24} H_{14} Cl_2 O_3$) (II). In the light of above observations following 4-aryloxymethylcoumarins using chloro/bromo substituents have been subjected to X-ray diffraction studies.

These compounds were subjected to the Claisen rearrangement at high temperature, which gave negative results [1]. Subsequently a number of 4-aryloxymethylcoumarins were synthesised as possible anti-microbial agents [2-4]. Introduction of biocompatible fragments like vanillin and paracetamol resulted in novel 4-aryloxymethylcoumarins, which exhibited anti-inflammatory, analgesic and interesting photophysical properties also [5,6]. 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 [7].

MATERIALS AND METHODS

6-chloro-4 bromomethylcoumarin and *p*-cresol.and Benzo-[*b*]-furanylcoumarin (II) is an oxygenated biheterocyclic system, synthesised by the reaction of 4-bromomethylcoumarin with salicylaldehyde, were synthesized in Department of Physics, Government College for Women, Kolar, Karnataka, India as per the designed scheme.

EXPERIMENTAL

The title compound (I) was synthesised by the reaction of 6-chloro-4 bromomethylcoumarin and *p*-cresol. The compound was purified by routine chemical methods, its observed melting point 180 ^{o} C and IR, NMR data was in agreement with literature report [3].

Benzo-[*b*]-furanylcoumarin (II) is an oxygenated biheterocyclic system, synthesised by the reaction of 4-bromomethylcoumarin with salicylaldehyde [1].

A number of derivatives of (II) were synthesised, screened for various biological activities [2, 3] subsequently use of *o*-hydroxy esters, ketones resulted in the synthesis of 3-substituted benzofuranylcoumarins exhibiting promising anti-inflammatory activity [4, 5]. The reaction was extended to *o*-hydroxyphenylketones which resulted in a number of 3-phenylderivatives.

CRYSTALLIZATION

Compound (I) has been grown by slow evaporation technique using ethyl acetate. 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 = 4.

Compound (II) Compound has been grown by slow evaporation technique using Chloroform. 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.

X-RAY DATA COLLECTION

The three dimensional intensity data (I) was collected using a crystal of size 0.30 × 0.20 × 0.20 mm mounted on an Bruker axs kappa apex2 [8] CCD 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 9957 were collected in the 2θ range 1.61 to 26.58°. The data was collected using ω and φ scans mode with h,-5 to 3, k, -11 to 11, and l, 31 to 31.The intensities were collected for Lorentz and polarisation effects. Among the 2137 unique reflections collected, 1502 observed reflections with $I \geq 2 \sigma (I)$. The space group $P2_1/c$ assigned from the systematic absences. The cell parameters are a = 15.3068(5), b = 6.9353(2), c = 14.9566(5) Å and β = $116.923(2)^0$. V = $1415.66(8)A^{\circ 3}$. Multi-scan absorption was carried out using SADABS [9]. The calculated absorption coefficient was 0.277 mm^{-1}.

The three dimensional intensity data was (II) collected using a crystal of size 0.24 × 0.18 × 0.13 mm mounted on an 'OXFORD DIFFRACTION XCALIBUR-S' Enhance MoKα X-ray Source' (λ = 0.71073 Å), At low (150K) temperature. The data was collected using ω and φ scans mode was collected in the 2θ range 3.51 to 25.00°. Among 14280 measured reflections of which 3353 independent reflections and 2116 reflections with $I > 2\sigma(I)$. With h,-18 to 20, k, -18 to 17, l, - 8 to 20. The crystals of the compound crystallize in Monoclinic with space group $P2_1/c$ having 4 molecules in the unit cell of dimensions crystal system a = 17.1293(12) Å, b = 15.2407(12) Å, c = 7.4419(6) Å and β = 101.066(7) °. V= $1906.7(3)A^{\circ 3}$. Multi-scan absorption was carried out using SADABS [8]. The calculated absorption coefficient was 0.365 mm^{-1}

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SHELXS-97 [9]. The position of all non-hydrogen atoms were revealed in the best E-map. Then refined using the program SHELXL-97 [10] by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R (F) = 0.0928, $wR(F^2)$ = 0.1387. 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 $w=1/[\sigma^2(Fo^2) + (0.0467P)^2+1.203P]$ where $P= (Fo^2+2Fc^2)/3$. The parameters at the end of final refinement were R (F) = 0.0533, $wR(F^2)$ = 0.1698. The minimum and maximum electron densities from difference Fourier map are 0.532 and 0.971 $e.A^{-3}$ respectively.

The structure was solved by direct methods using SHELXS-97 [9]. The position of all non-hydrogen atoms were revealed in the best E-map. Then refined using the program SHELXL-97 [10] by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R (F) = 0.0786, $wR(F^2)$ = 0.1111. 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 $w=1/[\sigma^2(Fo^2)+(0.0622P)^2+0.000P]$ where $P= (Fo^2+2Fc^2)/3$. The parameters at the end of final refinement were R (F) = 0.0477, $wR(F^2)$ = 0.1040. The minimum and maximum electron densities from difference Fourier map are 0.9176 and 0.9541 $e.A^{-3}$ respectively.

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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 [10] 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.

Molecule (I) is planar and individual coumarin and phenoxy moieties are planar. The phenoxy moiety is oriented anti periplanar with respect to the coumarin ring as indicated by the C7-C10-O3-C11 angle of 179.97°. The C10-O3 band is cis with respect to the coumarin ring (C5-C4) double bond is almost eclipsed with the dihedral angle of 5.3° between C8-C7-C10-O3. A significant bond deviation is observed at C5-C7 (1.449Å) due to the bridging of α pyrone ring and benzene ring at C5 carbon atom and also a substituent present on C7 carbon atom. This is also reflected at C8-C9 and C7-C10 due to attachment of oxygen atom at C9 carbon atom and a phenoxy group at C10 carbon atom respectively.

A significant bond angle of deviation is observed at C6-C5-C4 (117.91°) this is due to the flexing of α-pyrone ring and benzene ring at C5 and C6 carbon atoms. This is also reflected at C6-C5-C7 (117.61°). Another significant bond angle of deviation is observed at C15-C14-C13 (117.46°) due to presence of electron releasing methyl group on C14 carbon atom which makes repulsion of electrons. One more positive bond angle of deviation observed at C6-O1-C9 due to delocalisation of lone pair of electrons on the O1 atom which is responsible by benzene ring at C6 position and O2 present on C9 carbon atom. The molecule shows spatial proximity between H1-Cl1 of 2.880 Å. In addition to these there is a strong C-H…Cl hydrogen bond stabilizes the structure thus forms the sheet like arrangement of the molecules.

This molecule (II) has three ring systems which are aromatic. The coumarin and the phenyl moieties are linked to the vicinal carbons at C2 and C3 (C2-C16) of the benzofuran ring. Hence it is likely that the molecule is forced to adopt a non-planar arrangement to reduce the interelectronic repulsions. Coumarin and benzofuran rings are oriented at an angle of 40° whereas the phenyl ring is oriented at angle of 45° with respect to benzofuron moiety. Thus the molecule adopts a non-planar arrangement. A significance deviation in bond angle is observed at C24-O3-C11 (105.7°) this is due to the presence of lone pair of electrons on O3 atom which makes the repulsion between bond pair- lone pair electrons. Another deviation on bond angle is observed at O1-C1-C2 (116°). This is due to presence of oxygen atom on C1 atoms which is more electronegative than carbon and contain a lone pair of electrons on it. Another signification deviation is finding at C3-C2-C1. This is due to branching at C3 and presence of O2 on C1 atom which makes the electronic attracting less.

There is a deviation is find at C10-C4-C5 (116.9°). This is due to bridging between α Pyrone ring and toluene ring at C4 and C10 position. This is also reflected deviation at C10-C4-C3 (117.7°). There is another deviation is occurred at C11-C12-C19 (105.8°). This is account of branching at C11 and C12 and bridging at C19 these makes reducing the bond angle this is also reflected at C24-C19-C12 and at C23-C24-C19.

The interactions showing chlorine is found to have much significance in packing of molecules and stabilizing the molecular structure of the compound. It is interesting to observe that both Cl atoms of phenyl rings were interacting with Cl…Cl contacts (3.422Å) also forming a C-H…Cl interactions. However there is a C-H…O interaction between the molecules. Thus Cl…Cl interactions found to be important in stabilizing the structure. The molecules oriented parallel to each other.

Table 1: Crystal data and structure refinement

DATA	COMPOUND I	COMPOUND II
Empirical formula	$C_{17} H_{13} Cl O_3$	$C_{24} H_{14} Cl_2 O_3$
A	15.3068(5) Å	17.1293(12) Å
B	6.9353(2) Å	15.2407(12) Å
C	14.9566(5) Å	7.4419(6) Å
B	116.923(2) °	101.066(7)°
Volume	1415.66(8) $Å^3$	1906.7(3) $Å^3$
Crystal system	Monoclinic	Monoclinic
Formula weight	300.72	421.25
Space group	*P21/c*	*P 21/c*
F(000)	624	864
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ= 0.71073Å)
Z	4	4
Absorption coefficient	0.277 mm^{-1}	0.365 mm^{-1}
Calculated density	1.411 Mg/m^3	1.467 Mg/m^3
No. Parameters	191	263
R-obs	0.0533	0.0477
wR_2 (all)	0.1387	0.1040
Theta range for data collection	1.49 to 29.16 °	3.51 to 25.00°
$h_{min, max}$; $k_{min, max}$; $l_{min, max}$	-20<=h<=20, -9<=k<=6, -20<=l<=20	-18<=h<=20, -18<=k<=17, -8<=l<=8
Max. and min. Transmission	0.967 and 0.932	0.9541 and 0.9176
Goof(S)	1.081	0.902
No. Unique reflections.	3818	3353
Temperature	293(2) K	150(2) K
Largest diff. peak and hole	0.269 and -0.216 $e.A^{-3}$	0.586 and 0.225 $e.A^{-3}$

Table 2(Ia): Bond lengths [A°]

Atom1-atom2	Angle
C(1)-C(2)	1.365(3)
C(1)-C(6)	1.377(3)
C(2)-C(3)	1.385(3)
C(3)-C(4)	1.371(3)
C(3)-Cl(1)	1.731(2)
C(4)-C(5)	1.394(3)
C(5)-C(6)	1.392(2)
C(5)-C(7)	1.449(2)
C(6)-O(1)	1.367(2)
C(7)-C(8)	1.336(3)
C(7)-C(10)	1.495(2)
C(8)-C(9)	1.445(3)
C(9)-O(2)	1.199(2)
C(9)-O(1)	1.369(3)
C(10)-O(3)	1.411(2)
C(11)-O(3)	1.375(2)
C(11)-C(12)	1.375(3)
C(11)-C(16)	1.381(3)
C(12)-C(13)	1.387(3)
C(13)-C(14)	1.380(3)
C(15)-C(16)	1.381(3)

Table 2(Ib): Bond lengths [A°]

Atom1-atom2	Angle
Cl(1)-C(16)	1.743(3)
Cl(2)-C(21)	1.744(3)
O(1)-C(1)	1.374(3)
O(1)-C(10)	1.383(3)
O(2)-C(1)	1.202(3)
O(3)-C(24)	1.373(3)
O(3)-C(11)	1.398(3)
C(1)-C(2)	1.440(4)
C(2)-C(3)	1.349(4)
C(3)-C(4)	1.458(4)
C(3)-C(11)	1.463(4)
C(4)-C(10)	1.389(4)
C(4)-C(5)	1.394(4)
C(5)-C(6)	1.385(4)
C(5)-H(5)	0.9500
C(6)-C(8)	1.395(4)
C(6)-C(7)	1.495(4)
C(8)-C(9)	1.372(4)
C(9)-C(10)	1.377(4)
C(11)-C(12)	1.366(4)
C(12)-C(19)	1.449(4)
C(12)-C(13)	1.474(4)
C(13)-C(18)	1.389(4)
C(13)-C(14)	1.399(4)
C(14)-C(15)	1.374(4)
C(15)-C(16)	1.379(4)
C(16)-C(17)	1.374(4)
C(17)-C(18)	1.388(4)
C(19)-C(24)	1.381(4)
C(19)-C(20)	1.394(4)
C(20)-C(21)	1.382(4)
C(21)-C(22)	1.394(4)
C(22)-C(23)	1.374(4)
C(23)-C(24)	1.381(4)

Table 2(IIa): Bond lengths [A°]

Atom1-atom2-atom3	Angle
C(2)-C(1)-C(6)	119.81(19)
C(4)-C(3)-C(2)	121.8(2)
C(4)-C(3)-Cl(1)	119.73(16)
C(2)-C(3)-Cl(1)	118.47(17)
C(3)-C(4)-C(5)	119.56(18)
C(6)-C(5)-C(4)	117.91(17)
C(6)-C(5)-C(7)	117.61(18)
C(4)-C(5)-C(7)	124.48(16)
O(1)-C(6)-C(1)	116.47(17)
O(1)-C(6)-C(5)	121.71(18)
C(1)-C(6)-C(5)	121.8(2)
C(8)-C(7)-C(5)	119.38(16)
C(8)-C(7)-C(10)	122.52(17)
C(5)-C(7)-C(10)	118.09(16)
C(7)-C(8)-C(9)	122.34(18)
O(2)-C(9)-O(1)	116.54(18)
O(2)-C(9)-C(8)	126.4(2)
O(1)-C(9)-C(8)	117.07(17)
O(3)-C(10)-C(7)	109.05(15)
O(3)-C(11)-C(12)	124.69(16)
O(3)-C(11)-C(16)	115.23(17)
C(12)-C(11)-C(16)	120.08(17)
C(11)-C(12)-C(13)	119.20(18)
C(14)-C(13)-C(12)	121.9(2)
C(15)-C(14)-C(13)	117.46(18)
C(15)-C(14)-C(17)	121.8(2)
C(13)-C(14)-C(17)	120.7(2)
C(14)-C(15)-C(16)	122.1(2)
C(15)-C(16)-C(11)	119.2(2)
C(6)-O(1)-C(9)	121.85(15)
C(11)-O(3)-C(10)	116.67(14)

Table 2(IIb): Bond angles [°]

Atom1-atom2 –atom3	Angle
C(1)-O(1)-C(10)	121.9(2)
C(24)-O(3)-C(11)	105.7(2)
O(2)-C(1)-O(1)	117.5(3)
O(2)-C(1)-C(2)	126.3(3)
O(1)-C(1)-C(2)	116.2(2)
C(3)-C(2)-C(1)	123.7(3)
C(2)-C(3)-C(4)	118.2(2)
C(2)-C(3)-C(11)	118.8(3)
C(4)-C(3)-C(11)	122.9(2)
C(10)-C(4)-C(5)	116.9(3)
C(10)-C(4)-C(3)	117.7(3)
C(5)-C(4)-C(3)	125.4(3)
C(6)-C(5)-C(4)	122.5(3)
C(5)-C(6)-C(8)	117.7(3)
C(5)-C(6)-C(7)	120.8(3)
C(8)-C(6)-C(7)	121.5(3)
C(9)-C(8)-C(6)	121.3(3)
C(8)-C(9)-C(10)	119.1(3)
C(9)-C(10)-O(1)	116.1(2)
C(9)-C(10)-C(4)	122.1(3)
O(1)-C(10)-C(4)	121.8(3)
C(12)-C(11)-O(3)	111.3(2)
C(12)-C(11)-C(3)	135.9(3)
O(3)-C(11)-C(3)	112.6(2)
C(11)-C(12)-C(19)	105.8(2)
C(11)-C(12)-C(13)	128.2(2)
C(19)-C(12)-C(13)	125.9(2)
C(18)-C(13)-C(14)	118.4(2)
C(18)-C(13)-C(12)	120.2(3)
C(14)-C(13)-C(12)	121.4(3)
C(15)-C(14)-C(13)	120.8(3)
C(14)-C(15)-C(16)	119.3(3)
C(17)-C(16)-C(15)	121.7(3)
C(17)-C(16)-Cl(1)	119.4(2)
C(15)-C(16)-Cl(1)	118.9(2)
C(16)-C(17)-C(18)	118.6(3)
C(17)-C(18)-C(13)	121.2(3)
C(24)-C(19)-C(20)	119.3(3)
C(24)-C(19)-C(12)	106.3(2)
C(20)-C(19)-C(12)	134.4(2)
C(21)-C(20)-C(19)	117.1(2)
C(20)-C(21)-C(22)	122.4(3)
C(20)-C(21)-Cl(2)	119.9(2)
C(22)-C(21)-Cl(2)	117.7(2)
C(23)-C(22)-C(21)	120.9(3)
C(22)-C(23)-C(24)	116.1(3)
O(3)-C(24)-C(23)	124.9(2)
O(3)-C(24)-C(19)	111.0(2)
C(23)-C(24)-C(19)	124.2(2)

Table (3I): Dihedral angles formed by LSQ-planes

Plane - Plane	Angle (°)
1 2	2.08(0)
1 3	11.38(0)
2 3	9.35(0)

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

Plane - plane	Angle
1 2	36.01(5)
1 3	42.70(6)
2 3	43.68(7)

Table (4 I): Hydrogen bonding geometry

(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°
C4-H4…O4^{i}	0.930(0)	2.691(2)	3.553(2)	154
C10-10B…O2^{i}	0.970(0)	2.474(2)	3.303(2)	143
C12-12B…O2^{i}	0.930(0)	2.667(2)	3.402(2)	136
C1-H1…Cl^{ii}	0.930(0)	2.880(1)	3.693(1)	145

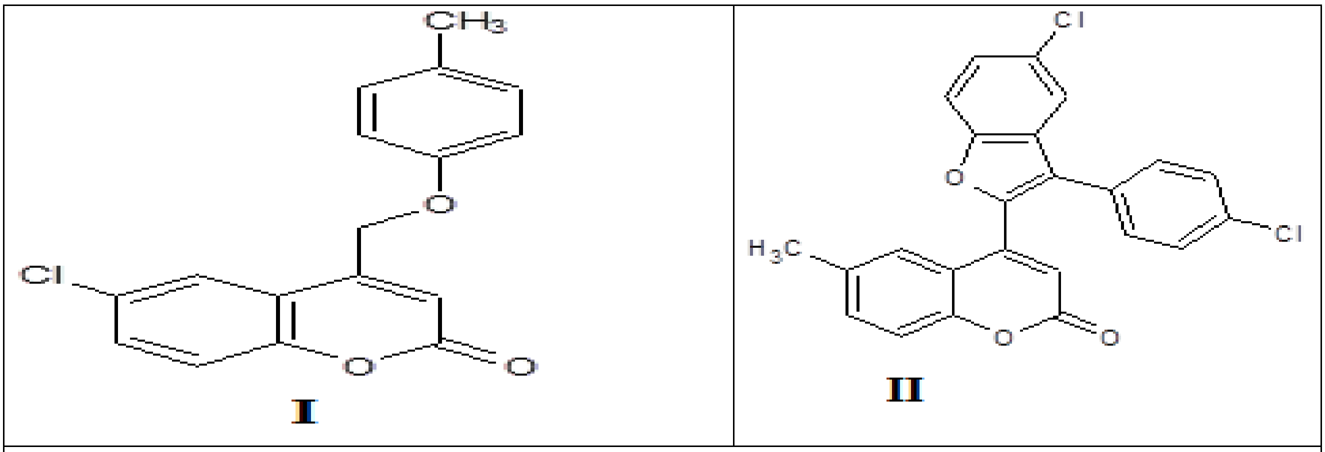
Equivalent positions: (i) x,-y+1/2,+z-1/2 (ii) x,-y+1/2,+z+1/2

Table (4 II): Hydrogen bonding geometry

(D-H…A)	(D-H) Å	(H…A)Å	(D….A)Å	(D-H…A)°
C18-H18 ...Cl2^{i}	0.950(0)	2.909(2)	3.713(2)	143
C20-H20 ...Cl1^{ii}	0.950(0)	2.878(2)	3.685(1)	143
C23-H23 ...O2^{iii}	0.950(0)	2.949(2)	3.781(2)	147

Equivalent positions:

(i) x,-y+1/2,+z-1/2
(ii) -x+1,-y,-z
(iii) -x+2,+y+1/2,-z+1/2



I

II

Fig. 1: Scheme of title compound I and II

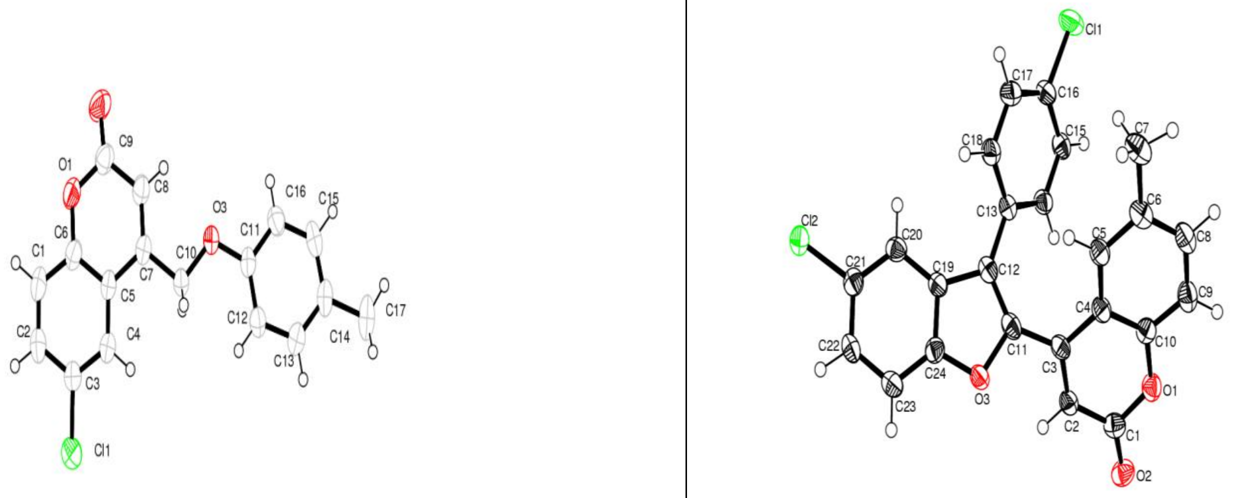


Fig. 2: ORTEP diagram of the title molecule with 50% probability displacement ellipsoids with-H atoms of I and II

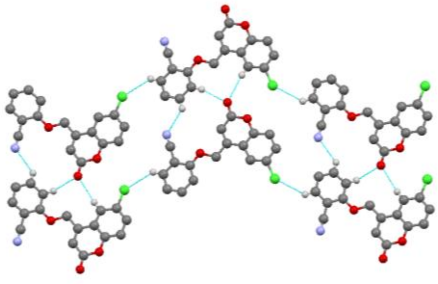


Fig. 3I: Packing of the molecules showing C-H…O and C-H…Cl hydrogen bonding.

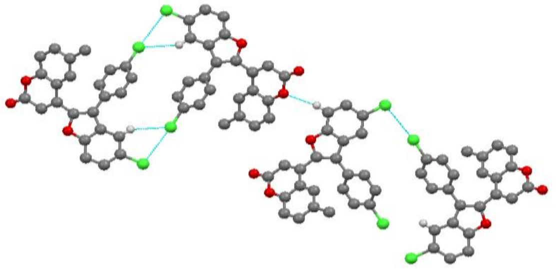


Fig. 3I:I Packing of the molecules showing C-H…O and C-H…Cl hydrogen bonding.

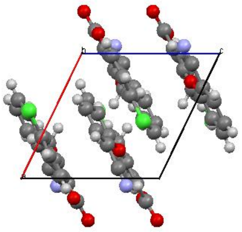
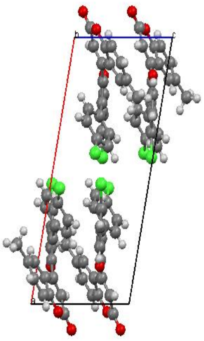
	

Fig. 4I: Packing diagram viewed down b-axis and molecules oriented as parallel layers along c-axis..	**Fig. 4II: Packing diagram viewed down b-axis.**

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