SUMMARY

Crystallography is an essential tool to know the structure of a molecule, and to understand its functions. X-ray crystallography provides a means to determine the molecular structure of a crystal and analyze the pattern of diffraction resulting from the interaction of X-rays with crystals. The crystal is essentially a stack of identical blocks and the factors that can be used to interpret various applications of the molecules on the basis of interactions. The crystallographic study provides not only the knowledge about the conformation, but also about the stereo-chemical facts, the most stable conformation of the molecules, interactions like hydrogen bonds and packing of the molecules in the solid state.

In the thesis, we reported here a synthesis and characterization and crystal structure analysis of a few calamatic liquid crystals, the extra interest is paid to the coumarin based compounds. In the path of synthesis of the targeted molecule we will come across a few interesting intermediate compounds, they are crystallographically analyzed and reported in separate chapters. It has more than two rigid cores and linking groups, alkyl chains on both the ends. Our one of the objectives of the work is to synthesis and characterization of calamatic liquid crystals. In particular, we are interested in coumarin based liquid crystals by replacing benzene rigid core of other rigid cores, off course coumarin core/moiety and -COO- linking group. We achieved our objective and the details of the work are reported in this thesis.

Chapter 3 describes the review of literature, materials and methods, results and discussion, structural features of two liquid crystals. In brief this chapter highlights the crystal structure analysis of symmetric napthalene-2,6-diyl bis (4-hydroxy benzoate) (3a) and 4-cyanophenoxy-carbonyl-phenyl 4’-(trimethylsilyl)-ethynyl-benzoate (3b) including their liquid crystal characterization. The crystallographic data is analyzed and
compared; further the idea used for the structure is used to develop coumarin based molecules (aim of this thesis) discussed in the other chapters. In brief, a rod like liquid crystals (3a) and (3b) are synthesized, characterized and analyzed, their crystallographic information are reported. In (3a) the terminal two heptyloxybenzene coupled naphthalene molecule exhibited nematic phase and (3b) trimethylsilyl coupled three phenyl ring compound exhibited enantiotropic Smectic A phase and POM studies were done to observe the texture. The single crystal X-ray diffraction studies of (3a) show that the compound is crystallizes in triclinic $P_i$ space group with unit cell dimension $a=5.569(3)\,\text{Å}$, $b=10.540(5)\,\text{Å}$, $c=15.254(9)\,\text{Å}$, $\alpha=73.434(18)^\circ$, $\beta=80.807(19)^\circ$ and $\gamma=82.02(2)^\circ$, $V=843.1(8)\,\text{Å}^3$. The dihedral angle between the naphthalene ring system and the benzene ring is $63.63(2)^\circ$. The crystal structure is stabilized by $\text{C–H}\cdots\pi$ interactions.

The single crystal X-ray diffraction studies of (3b) show that the compound is crystallizes in triclinic, $P_i$ space group with unit cell dimension $a=5.9577(2)\,\text{Å}$, $b=8.0398(3)\,\text{Å}$, $c=25.8842(9)\,\text{Å}$, $\alpha=86.096(2)^\circ$, $\beta=89.912(2)^\circ$ and $\gamma=72.919(2)^\circ$, $V=1182.16(7)\,\text{Å}^3$. The crystal structure is stabilized by $\text{C–H}\cdots\text{O}$ intra-molecular and $\text{C–H}\cdots\pi$ interactions and also by $\pi\cdots\pi$ interactions $[\text{centroid–centroid separation} = 3.806 \,(3) \,\text{Å}]$. The related reference is listed at the end of the chapter.

Chapter 4 describes the review of literature, materials and methods, results and discussion, structural features four single crystals. In brief, this chapter highlights the effect of ester link present in the crystal structures of Methyl 4-benzyloxy-2-hydroxybenzoate (4a), 4-Nitrophenyl 4-hydroxy-3-methylbenzoate (4b), bis(4-methoxyphenyl) malonate (4c) and 4′-Cyanobiphenyl-4-yl 7-diethylamino-2-oxo-2H-chromene-3-carboxylate (4d). The single crystal X-ray diffraction studies of (4a) show that the compound is crystallizes in triclinic, $P_i$ space group with unit cell dimension
SUMMARY

In molecular structure, the dihedral angle between the benzene rings is 67.18 (8) Å. The Ca—Cm—O—Ca (a = aromatic and m = methylene) torsion angle is 172.6 (3) Å and an intramolecular O—H···O hydrogen bond generates an S(6) ring. In the crystal, molecules are linked by C—H···O hydrogen bonds into zigzag chains propagating in [001] and C—H···π interactions also occur.

The single crystal X-ray diffraction studies of (4b) show that the compound is crystallizes in monoclinic, C2/c group with unit cell dimension a=42.313 (6) Å, b= 8.0047 (11) Å, c= 16.1078(18) Å, α=90°, β=105.819(4)° and γ=90°, V=5249.2(12) Å³. The asymmetry unit contains two independent molecules in which the dihedral angles between the benzene rings are 89.27(16) Å and 77.14(12) Å. In the crystal, molecules are linked by O—H···O hydrogen bonds, generating C(8) chains propagating in [010] for one molecule and [001] C(8) chains for the other. The chains are connected by C—H···O hydrogen bonds and π – π interactions [shortest centroid–centroid distance = 3.5908 (12) Å, generating a three-dimensional network.

The single crystal X-ray diffraction studies of (4c) show that the compound is crystallizes in orthorhombic, Pbcn space group with unit cell dimension a=5.4307 (19) Å, b= 8.131 (3)Å, c= 36.149 (10)Å, α=90°, β=90° and γ=90°, V= 1596.3 (9)Å³. The molecules of show two fold rotation symmetry, for which the 2-fold rotation crystallographic axis passes through the C9 atom (with symmetry code -x, y, -z+1/2). The asymmetric unit of the title compound contains half molecule. The carbonyl oxygen atom is disordered over two positions due to crystallographic 2- fold rotation axis (orientational disorder), the occupancy ratio being 0.63 (3):0.37 (3). The dihedral angle between the benzene rings in the two halves of the molecule is 79.31 (12)°. Further, the dihedral angle between the central –CH2–C(O)–O– segment and the phenyl ring is 86.41 (6)°. The
methoxy group is approximately coplanar with the attached benzene ring, the C1—O1—C2—C3 torsion being 3.76 (1)°.

In the crystal structure, the molecules are connected via C9—H9···O3 intermolecular interactions running into C(4) chains along crystallographic a and b axis, thus forming sheets in the ab plane. These sheets are further stabilized by C4—H4···π and C7—H7···π interactions (where Cg is the centroid of the phenyl ring) along [010], and thus, a two dimensional architecture is observed.

The single crystal X-ray diffraction studies of (4d) show that the compound is crystallizes in triclinic, P1 space group with unit cell dimension a=9.652 (3), b= 10.252 (4) Å, c= 11.121 (4) Å, α=87.214 (10), β=86.358 (10)° and γ= 84.348 (11)°, V= 1091.9 (6) Å³.

In molecular structure of the (4d) the dihedral angles between the central benzene ring and the cyanobenzene ring and the 2H-coumarin ring system (r.m.s. deviation = 0.014 Å) are 22.95 (11) and 75.59 (8)°, respectively. Both terminal C atoms of the pendant diethylamino group lie to the same side of the coumarin ring system [deviations = 1.366 (2) and 1.266 (2) Å]. In the crystal, molecules are linked by C—H···O and C—H···N hydrogen bonds and a C—H···π interaction, generating a three-dimensional network. The related reference is listed at the end of the chapter.

Chapter 5 describes the review of literature, materials and methods, results and discussion and structural features of two single crystals 4-Iodophenyl-2-oxo-2H-chromene-3-carboxylate (5a) and 4-Bromophenyl-2-oxo-2H-chromene-3-carboxylate (5b). The single crystal X-ray diffraction studies of (5a) show that the compound is crystallizes in monoclinic, P21/c space group with unit cell dimension a=16.2728 (6) Å, b= 7.2769 (2) Å, c= 12.7340(5) Å, α=90°, β=111.898(2)° and γ=90°, V= 1399.11(9) Å³. In the crystal, molecules are linked by C—H···π interaction, generating a three-dimensional network.
The single crystal X-ray diffraction studies of (5b) show that the compound is crystallizes in monoclinic, \(P2_1/c\) space group with unit cell dimension \(a=16.0782(10)\ \text{Å}, b=7.2618(4)\ \text{Å}, c=12.7396(8)\ \text{Å}, \alpha=90^\circ, \beta=113.311 (4)^\circ \text{and } \gamma=90^\circ, \ V=1366.01(15)\ \text{Å}^3\). The dihedral angle between coumarin ring and bromo benzene ring is \(25.86\ (2)^\circ\). Further, the torsions C9—C8—C10—O3, O3—C10—O4—C11 and C12—C11—O4—C10 have values \(27.6(4)^\circ, 6.3(3)^\circ\) and \(124.6(2)^\circ\) respectively. The structural parameters are compared with other crystals. The related reference is listed at the end of the chapter.

Chapter 6 describes the review of literature, materials and methods, results and discussion and structural features of three single crystals 4-(meth)oxyphenyl 2-oxo-2H-chromene-3-carboxylate(6a), 4-(butoxy)phenyl 2-oxo-2H-chromene-3-carboxylate(6b) 4-(Octyloxy) phenyl 2-oxo-2H-chromene-3-carboxylate (6c). The single crystal X-ray diffraction studies of (6a) show that the compound is crystallizes in Orthorhombic, \(P2_12_12_1\) space group with unit cell dimension \(a=6.2648(18)\ \text{Å}, b=10.435(3)\text{Å}, c=20.621(7)\text{Å}, \alpha=90^\circ, \beta=90^\circ \text{and } \gamma=90^\circ, \ V=1348.0(7)\text{Å}^3\). In the molecule the dihedral angle between the planes of the coumarin ring system (r.m.s. deviation =0.015 Å) and the benzene ring is 48.04 (10)Å. The central –OCO- group subtends a dihedral angle of 27.15 (11)Å with the coumarin ring system and 74.86(13) Å with the benzene ring. In the crystal, molecules are linked by C—H···O interactions, which generate a three-dimensional network. Very weak C—H···π interactions are also observed.

The single crystal X-ray diffraction studies of (6b) show that the compound is crystallizes in triclinic, \(P_\tau\) space group with unit cell dimension \(a=6.5697(4)\ \text{Å}, b=7.5325(5)\ \text{Å}, c=19.0140(14)\text{Å}, \alpha=91.251(5)^\circ, \beta=99.860(3)^\circ \text{and } \gamma =114.176(3)^\circ, \ V=841.29 (10)\ \text{Å}^3\). The dihedral angle between the planes of the coumarin ring system (r.m.s. deviation = 0.031 Å) and the benzene ring is 32.17(21)°. The central –OCO- group subtends a dihedral angle of 27.25 (12)° with the coumarin ring system and 59.42 (14)°
with the benzene ring. In the crystal, molecules are linked by C—H···O interactions, which generate a three-dimensional network. Further a π-π stacking.

The single crystal X-ray diffraction studies of (6c) show that the compound is crystallizes in Monoclinic, \(P2_1/n\) space group with unit cell dimension \(a=14.464(3)\,\text{Å}, b=6.7548(15)\,\text{Å}, c=21.381(01)\,\text{Å}, \alpha=90.0^\circ, \beta=91.663(8)^\circ\) and \(\gamma=90^\circ\), \(V=2088.0(8)\,\text{Å}^3\). In the molecular structure the 2H-chromene ring system is essentially planar, with a maximum deviation of 0.029 (2) \(\text{Å}\) from the best-fit mean plane incorporating both rings. The dihedral angle between the 2H-chromene ring system and the benzene ring is 21.00(1)Å. In the crystal, pairs of C—H···O hydrogen bonds generate an \(R_2^2(8)\) ring pattern. These contacts are bolstered by weaker bifurcated C—H···O hydrogen bonds. The structural parameters are compared with other crystals[13]. The related reference is listed at the end of the chapter.

Chapter 7 describes the review of literature, materials and methods, results and discussion Synthesis of eleven number of compounds(7a-7k) in which 4-(4-(Heptyloxy)benzoyloxy)phenyl 7-(trifluoromethyl)-2-oxo-2H-chromene-3-carboxylate (7e) and 4-(Decyloxy)phenyl 2-oxo-7-trifluoromethyl-2H-chromene-3-carboxylate (7k) are crystallographically analyzed. The single crystal X-ray diffraction studies of (7e) show that the compound is crystallizes in triclinic, \(P\) space group with unit cell dimension \(a=5.6810(3)\,\text{Å}, b=16.036(2)\,\text{Å}, c=16.2954(18)\,\text{Å}, \alpha=68.940(12)^\circ, \beta=88.914(6)^\circ\) and \(\gamma=88.486(7)^\circ\), \(V=1384.8\,(3)\,\text{Å}^3\). The molecule exhibits enantiotropic SmA, nematic phase transitions at 520.2(2.0), 522.7(2.7) on heating and at 519.6(2.0), 522.1(2.9) on cooling. The three F atoms of the –CF3 group are disordered over two sets of sites with occupancy factors 0.62(3):0.38(3). The crystal structure is stabilized by two pairs of C8—H8···O3 and C3—H3···O6 hydrogen bonds form inversion dimers and generate \(R^2_2(10)\) and \(R^2_2(30)\) ring patterns respectively. The C16—H16···O6 contact and C—H···Cg1 (centroid
of C12—C17) and C—H···Cg2 (centroid of C19—C24) interactions further strengthen the packing.

The single crystal X-ray diffraction studies of (7k) show that the compound is crystallizes in triclinic, P21/c space group with unit cell dimension a=27.85 (3) Å, b=9.281 (10) Å, c= 9.981 (11) Å, α=90°, β=94.849 (18)° and γ= 90°, V= 2571 (5) Å³. In the three F atoms of the –CF3 group are disordered over two sets of sites with occupancy factors 0.71 (4):0.29 (4). The crystal structure is characterized by intermolecular C10—H10···O3 hydrogen bonds that form inversion dimer and generate a R22(10) ring pattern. C27—H27···F1 hydrogen bonds then link the dimer into chains along a. The structure is further stabilized by C3—H3···Cg1, C6—H6···Cg2 and C16—H16···Cg2 interactions. The structural parameters are compared with other crystals. The related references are listed at the end of the chapter.

**Future work:** VGST Government of Karnataka has sanctioned 30lackh rupees project to extend the work to develop liquid crystals as a photovoltaic materials.