Abstract

The research work carried out during 2009-2012 comprises of crystal and molecular structure analysis of benzophenone derivative, quinoline derivative, salicylic acid derivative, imidazopyridine derivative, hydantoin derivative, naphthalene derivative, benzofuran derivative and two liquid crystals. The results have been compiled in the thesis entitled “Crystal and molecular structure analysis of two liquid crystals and few organic molecules of medicinal interest”. The single crystal X-ray diffraction data of six crystals were collected at Solid State Structural Chemistry Unit, IISc, Bangalore, India, one data at Sophisticated Analytical Instrument Facility, IIT, Chennai, India, one data at National Single Crystal Diffractometer Facility, School of Chemistry, Central University, Hyderabad, India, and one data at Department of chemistry, Pondicherry University, Pondicherry, India.

Introduction

This chapter gives a brief introduction to the various classes of compounds studied along with the schematic diagrams of each molecule. The importance of these compounds in the therapeutic field and their applications are also mentioned in brief.

X-ray crystallography

The second chapter gives details of the X-ray diffraction phenomenon. It elucidates the use of X-rays in the single crystal X-ray diffraction as a technique to study the crystal and molecular structures of small molecules. The chapter also briefs about the working and details of the two instruments viz., Bruker SMART CCD area-detector diffractometer [1] and Oxford Diffraction Xcalibur diffractometer [2] that were used for data collection.
**Benzophenone derivative**

This chapter encompasses the crystal and molecular structure of benzophenone derivative. IUPAC name, crystal class, space group, empirical formula and structural analysis of this compound are summarized below:

**Ethyl 2-(4-benzoyl-2,5-dimethylphenoxy)acetate (1).**

The compound \( (C_{19}H_{20}O_4) \), crystallizes in the Triclinic space group \( P\overline{T} \) with cell dimensions \( a = 8.148 \) (4)Å, \( b = 8.635 \) (4)Å, \( c = 13.029 \) (7)Å, \( \alpha = 84.054 \) (8)°, \( \beta = 81.176 \) (8)°, \( \gamma = 66.559 \) (7)°, \( V = 830.2 \) (7)Å\(^3\) and \( Z= 2 \). The intensity data were collected by \( \omega \) and \( \varphi \) scan technique using a Bruker SMART CCD area-detector diffractometer [1] with monochromatic Mo \( K\alpha \) radiation (\( \lambda=0.71073\)Å). The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure (SHELXL-97) [4] to final values of \( R_1 = 0.057, wR_2 = 0.173 \) for 2630 observed reflections with I >2σ (I). Here The dihedral angle between least-squares planes (two phenyl rings) is 69.04 (11)°. The crystal structure features intermolecular non-classical C-H···O hydrogen bonds [5].

**Quinoline derivative**

This chapter encompasses the crystal and molecular structure of quinoline derivative. IUPAC name, crystal class, space group, empirical formula and structural analysis of this compound are summarized below:

**3,4-Dimethoxybenzaldehyde[2,8-bis-(trifluoromethyl)quinolin-4-yl]hydrazone (2).**

The compound \( (C_{20}H_{15}F_6N_3O_2) \), crystallizes in the Triclinic space group \( P\overline{T} \) with cell dimensions \( a = 7.0359(6)\)Å, \( b =8.9617(8)\)Å, \( c = 15.5315(14)\)Å, \( \alpha = 90.154(1) \) °, \( \beta = 93.951(1)\)°, \( \gamma = 96.449(1)\)°, \( V = 970.75(15)\)Å\(^3\) and \( Z= 2 \). The intensity data were collected by \( \omega \) and \( \varphi \) scan technique using a Bruker SMART CCD area-detector diffractometer [1] with monochromatic Mo \( K\alpha \) radiation (\( \lambda=0.71073\)Å). The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure (SHELXL-97) [4] to final values of \( R_1 = 0.060, wR_2 = 0.175 \) for 2951 observed reflections with I >2σ (I). A very small dihedral angle \( 2.31(8)° \) between the quinoline system and the benzene ring indicates that these two systems are coplanar. In the crystal structure, intermolecular C-H···F hydrogen bonding
involving the trifluoromethyl and methine groups results in the formation of a three-dimensional ladder-type network [6]. In addition, a weak π-π interaction is observed between the benzene ring and benzene ring of quinoline, with a centroid-centroid distance of 3.586 (1)Å.

Salicylic acid derivative

This chapter encompasses the crystal and molecular structure of salicylic acid derivative. IUPAC name, crystal class, space group, empirical formula and structural analysis of this compound are summarized below:

**Methyl 5-Acetyl-2-Hydroxybenzoate (3).**

The compound (C\(_{10}\)H\(_{10}\)O\(_3\)), crystallizes in the Monoclinic space group \(P2_1/c\) with cell dimensions \(a = 8.8321(4)\,\text{Å},\ b = 7.5358(3)\,\text{Å},\ c = 14.8294(6)\,\text{Å},\ V = 959.12(7)\,\text{Å}^3,\ \beta = 103.650(4)^\circ\) and \(Z = 4\). The intensity data were collected by \(\omega\) and \(\phi\) scan technique using a Bruker SMART CCD area-detector diffractometer [1] with monochromatic Mo \(K\alpha\) (\(\lambda=0.71073\)Å) radiation. The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure (SHELXL-97) [4] to final values of \(R_1 = 0.0523,\ wR_2 = 0.1573\) for 1090 observed reflections with \(I > 2\sigma (I)\). The Phenyl ring system is slightly coplanar with the acetaldehyde group; the dihedral angle between the two planes is 5.68(15)\(^\circ\). The structure displays intermolecular O-H····O, C-H···O and intramolecular O-H···O hydrogen bonds [6].

Imidazopyridine derivative

This chapter encompasses the crystal and molecular structure of imidazopyridine derivative. IUPAC name, crystal class, space group, empirical formula and structural analysis of this compound are summarized below:

**N-(6-chloro-1-methyl-1H-imidazo[4,5-c]pyridin-4-yl)benzenesulfonamide (4).**

The compound (C\(_{13}\)H\(_{11}\)ClN\(_4\)O\(_2\)S), crystallizes in the Monoclinic, space group \(P2_1/c\) with cell dimensions \(a = 13.1045(4)\,\text{Å},\ b = 14.7259(5)\,\text{Å},\ c = 14.6953(6)\,\text{Å},\ \beta = 95.127(3)^\circ,\ V = 2824.49(17)\,\text{Å}^3\) and \(Z = 8\). The intensity data were collected by \(\omega\) scan technique using an Oxford Diffraction Xcalibur diffractometer [2] with monochromatic Mo \(K\alpha\) radiation (\(\lambda=0.71073\)Å). The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure...
(SHELXL-97) [4] to final values of $R_1 = 0.0365$, $wR_2 = 0.0983$ for 4489 observed reflections with $I > 2\sigma (I)$. There are two independent molecules in the asymmetric unit of the title compound, $C_{13}H_{11}ClN_4O_2S$. The imidazo-pyridine ring is not coplanar with the benzene ring system; the dihedral angle between the two planes being $62.32(8)^\circ$ and $80.80(9)^\circ$ in the two molecules. The crystal structure is characterized by intermolecular C-H···Cl, C-H···O and intermolecular N-H···N and C-H···O hydrogen bonding [6].

**Hydantoin derivative**

This chapter encompasses the crystal and molecular structure of hydantoin derivative. IUPAC name, crystal class, space group; empirical formula and structural analysis of this compound are here in summarised below:

$N\{3-[2-(4-Fluorophenoxy)ethyl]-2,4\text{-dioxo-1,3-diazaspiro}[4.5]\text{decan-7-yl}\}-4\text{methylbenzamide (5)}$.

The compound ($C_{24}H_{26}FN_3O_4$), crystallizes in the Triclinic, space group $P\bar{1}$ with cell dimensions $a = 9.1436 (17) \text{Å}$, $b = 10.103 (2)\text{Å}$, $c = 13.939 (2)\text{Å}$, $\alpha = 99.239 (15)^\circ$, $\beta = 106.550 (14)^\circ$, $\gamma = 107.417 (18)^\circ$, $V = 1134.5 (4)\text{Å}^3$ and $Z=2$. The intensity data were collected by $\omega$ scan technique using an Oxford Diffraction Xcalibur diffractometer [2] with monochromatic Mo $K\alpha$ radiation ($\lambda=0.71073\text{Å}$). The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least square procedure (SHELXL-97) [4] to final values of $R_1 = 0.052$, $wR_2 = 0.135$ for 2163 observed reflections with $I > 2\sigma (I)$. The two aromatic rings form a dihedral angle of $88.81(15)^\circ$. The cyclohexane ring adopts a chair conformation and the five-membered ring is essentially planar, with a maximum deviation from planarity of $0.041(2)\text{Å}$. The crystal structure displays intermolecular C-H···O and N-H···O hydrogen bonds [6].

**Naphthalene derivative**

This chapter encompasses the crystal and molecular structure of naphthalene derivative. IUPAC name, crystal class, space group, empirical formula and structural analysis of this compound are summarized below:
Abstract

1-Chloro-4-(3, 4-dichlorophenyl)-3,4-dihydronaphthalene-2-carbaldehyde (6).

The compound \((C_{17}H_{11}Cl_3O)\), crystallizes in the primitive monoclinic space group \(P2_1/c\) with cell dimensions \(a = 10.2969\) (5)Å, \(b = 10.8849\) (5)Å, \(c = 13.6144\) (7)Å, \(\beta = 91.436\) (5)°, \(V = 1525.43\) (13)Å³ and \(Z = 4\). The intensity data were collected by \(\omega\) scan technique using an Oxford Diffraction Xcalibur Diffractometer [2] with monochromatic Mo-\(K\alpha\) radiation \(\lambda = 0.71073\)Å. The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least square procedure (SHELXL-97) [4] to final values of \(R_1 = 0.050\), \(wR_2 = 0.149\) for 2143 observed reflections with \(I > 2\sigma (I)\). The dihydronaphthalene ring system is non-planar, the dihedral angle between the two fused rings being 10.87(13)°; it forms a dihedral angle of 81.45(10)° with the dichlorophenyl ring. The crystal structure features inter-molecular C-H…O hydrogen bonds [6].

**Benzofuran derivative**

This chapter encompasses the crystal and molecular structure of Benzofuran derivative. IUPAC name, crystal class, space group, empirical formula and structural analysis of this compound are summarized below:

1-(1-Benzofuran-2-yl)-3-(4-chlorophenyl)prop-2-en-1-one (7).

The compound \((C_{17}H_{11}ClO_2)\), crystallizes in the Triclinic space group \(P2_1/c\) with cell dimensions \(a = 15.9034\) (12)Å, \(b = 14.1393\) (12)Å, \(c = 5.9572\) (5)Å, \(\beta = 93.039\) (4)°, \(V = 1337.67\) (19)Å³ and \(Z = 4\). The intensity data were collected by \(\omega\) and \(\phi\) scan technique using a Bruker SMART CCD area-detector diffractometer [1] with monochromatic Mo-\(K\alpha\) radiation \(\lambda = 0.71073\)Å. The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure (SHELXL-97) [4] to final values of \(R_1 = 0.040\), \(wR_2 = 0.115\) for 2665 observed reflections with \(I > 2\sigma (I)\). The benzofuran ring system is almost planar (r.m.s. deviation = 0.011Å) and forms a dihedral angle of 10.53(6)° with the chlorophenyl ring. No significant intermolecular interactions are observed.

**Liquid crystals**

This chapter gives a brief introduction to the liquid crystals their properties and applications. This followed by the crystal and molecular structure analysis of two
nematic liquid crystals. IUPAC name, Crystal class, Space group and the structural analysis of each compound are summarized below:

1. 4-(Benzyloxy)phenyl4-hexadecyloxy-3-methoxybenzoate (8).

The compound (C\textsubscript{37}H\textsubscript{50}O\textsubscript{5}), crystallizes in the Triclinic space group P\overline{1} with cell dimensions \(a = 5.4507\) (2)Å, \(b = 9.7352\) (4) Å, \(c = 31.3738\) (14) Å, \(\alpha = 94.155\) (4)°, \(\beta = 94.261\) (4)°, \(\gamma = 95.576\) (4)°, \(V = 1647.02\) (12) Å\(^3\) and \(Z = 2\). The intensity data were collected by \(\omega\) scan technique using an Oxford Diffraction Xcalibur [2] diffractometer with mono-chromatic Mo \(K\alpha\) radiation (\(\lambda = 0.71073\)Å). The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure (SHELXL-97) [4] to final values of \(R_1 = 0.052\), \(wR_2 = 0.131\) for 2558 observed reflections with \(I > 2\sigma (I)\). The crystal structure of the title compound contains one molecule in the asymmetric unit. The central benzene ring makes dihedral angles of 39.72 (14) and 64.43 (13) with the benzyl and 3-methoxybenzoate rings, respectively. The crystal structure is stabilized by intermolecular C-H···π interactions involving the central benzene ring and the benzene ring closest to the aliphatic chain [6].

2. N-(4-heptylphenyl)acetamide (9).

The compound (C\textsubscript{15}H\textsubscript{23}NO), crystallizes in the Triclinic space group P-1 with cell dimensions \(a = 9.5432\) (4) Å, \(b = 17.3533\) (7) Å, \(c = 18.8570\) (7)Å, \(\alpha = 111.880\) (2)°, \(\beta = 92.552\) (3)°, \(\gamma = 91.206\) (3)°, \(V = 2892.6\) (2)Å\(^3\) and \(Z = 8\). The intensity data were collected by a Bruker SMART CCD area-detector diffractometer [1] with monochromatic Mo \(K\alpha\) radiation (\(\lambda = 0.71073\)Å). The structure was solved by direct methods (SHELXS-97) [3] and refined by full-matrix least squares procedure (SHELXL-97) [4] to final values of \(R_1 = 0.0580\), \(wR_2 = 0.1448\) for 4083 observed reflections with \(I > 2\sigma (I)\). The asymmetric unit contains four molecules. The aromatic rings and alkyl chains of the each molecules are non coplanar; the dihedral angles between phenyl rings and alkyl chains of molecules are 64.10(3)°, 30.5(5) °, 27.8(4)° & 73.4(3)° respectively. The molecular assembly in the structure is established by an intramolecular N-H···O & C-H···O, intermolecular N-H···O hydrogen bonds [6] and as well as C-H···π-electron ring C\textsubscript{8}(3) [C\textsubscript{10D}--C\textsubscript{15D}] interactions.
Summary

This chapter summarizes the results of the structure analyzed earlier. The molecular structures of similar compounds are compared. The effects of various substituents on the molecule are brought out.
References


