The thesis describes the results of synthetic and spectral studies on a large number of aromatic esters, substituted sulphonamides and the related compounds, such as aryl substituted benzoates and N-(aryl)-substituted benzenesulphonamides. It further describes the single-crystal X-ray structural studies of several of these compounds. The objective of the research is to correlate the bond and spectroscopic parameters of this class of compounds with their structures to explore the effect of substituents on the spectral and structural parameters of these compounds. This may eventually help in correlating these aspects of the compounds with their biological activities.

A great deal of work on the spectroscopic and structural aspects of aromatic esters, aryl sulphonamides and the related compounds needs to be done for correlating their reactivity with the chemical bond parameters. As a part of these efforts I have undertaken the synthetic, spectroscopic and single-crystal X-ray studies on several aromatic esters, substituted aryl sulphonamides and related compounds. 54 aromatic esters such as 2/3/4-halo/methyl-phenyl-2/3/4-chloro/methyl/methoxy benzoates of the configuration: i-XC₆H₄-CO-O-(j-YC₆H₄) (X = Cl, CH₃ or OCH₃; i = 2, 3, 4; Y = H, F, Cl, Br or CH₃; j = 2, 3, 4) have been prepared, characterized and their infrared spectra in the solid state and ^1H and ^13C NMR spectra in solution measured and correlated. The C=O absorption frequencies of aryl benzoates and aryl substituted benzoates have been compared with the corresponding benzanilides and substituted benzanilides. 36 N-(Dichloro/dimethyl-substituted-phenyl)-dichloro/dimethyl-benzenesulphonamides of the general formula, i-X-j-YC₆H₃SO₂NH(i-j-XC₆H₃) (where i-X-j-Y = 2,4-(CH₃)₂; 2-CH₃-4-Cl or 2,4-Cl₂ and i-j-X₂ = 2,3-(CH₃)₂; 2,4-(CH₃)₂; 2,5-(CH₃)₂; 2,6-(CH₃)₂; 3,4-(CH₃)₂; 3,5-(CH₃)₂; 2,3-Cl₂; 2,4-Cl₂; 2,5-Cl₂; 2,6-Cl₂; 3,4-Cl₂ or 3,5-Cl₂) and 15 N-substituted aryl sulphonamides of the configuration, 4-XC₆H₄SO₂NHR (X = H, F, Cl, Br or CH₃ and R = CH₃, C₂H₅ or C₄H₉) have also been prepared, characterised and their ^1H and ^13C NMR spectra in solution measured and correlated.

Further, single-crystal X-ray study of several of the above aromatic esters, aryl sulphonamides and related compounds have been determined and analysed. The compounds studied are, 21 aryl benzoates (phenyl benzoate, 3-chlorophenyl benzoate, 4-chlorophenyl benzoate, 3-methylphenyl benzoate, 4-bromophenyl benzoate,
2,3-dichlorophenyl benzoate, 2,6-dichlorophenyl benzoate, 3,4-dichlorophenyl benzoate, 2,3-dimethylphenyl benzoate, 2,4-dimethylphenyl benzoate, 2-chlorophenyl 4-methyl benzoate, 3-chlorophenyl 4-methylbenzoate, 4-chlorophenyl 4-methylbenzoate, 2-methylphenyl 4-methylbenzoate, 3-methylphenyl 4-methylbenzoate, 4-methylphenyl 4-methylbenzoate, 2,4-dichlorophenyl 4-methylbenzoate, 2,6-dichlorophenyl 4-methylbenzoate, 3,5-dichlorophenyl 4-methylbenzoate, 4-chlorophenyl 4-chlorobenzoate, 4-methylphenyl 4-chlorobenzoate), five aryl sulphonamides (N-(3-chlorophenyl)benzenesulphonamide, N-(2-methylphenyl)benzenesulphonamide, N-(2,3-dimethylphenyl)benzenesulphonamide, N-(2,6-dimethylphenyl)benzenesulphonamide and N-(3,5-dichlorophenyl)benzenesulphonamide), 4,6-dimethylbenzene-1,3-disulphonamide, 3,4-dichlorobenzene-sulphonamide and potassium 4-chlorobenzenesulphonate.

Infrared spectral measurements were made on FT-IR spectrophotometers. The resolution was set to 4 cm$^{-1}$ and the scanning range was from 400 to 4000 cm$^{-1}$. The spectra were measured in the solid state in the form of KBr pellets. The NMR spectral measurements were carried out on a BRUKER AVANCE II 400MHz FT-NMR spectrometer. Both $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$/DMSO with Me$_4$Si as internal standard.

Single crystals of sulphonamides and benzoates were obtained for structure determinations and measurements were made on CAD-4 Diffractometer or Oxford Xcalibur Diffractometer at room temperature. The details of experimental conditions and the programs/softwares used in the crystal structure determinations were

**Measurement device**: Enraf-Nonius CAD-4 Diffractometer, 1996; Xcalibur Diffractometer with Sapphire CCD detector (Oxford Diffraction, 2007)

**Data collection**: CAD-4-PC (Nonius, 1996); CrysAlis CCD (Oxford Diffraction, 2007);

**Cell refinement**: CAD-4-PC (Nonius, 1996); CrysAlis RED (Oxford Diffraction, 2007);

**Data reduction**: REDU4 (Stoe & Cie, 1987); CrysAlis RED (Oxford Diffraction, 2007);

**Structure solution**: SHELXS97 (Sheldrick, 2008); SHELXL97 (Sheldrick, 2008);
Structure refinement: PLATON (Spek, 2003); ORTEP-3 (Farrugia, 1997);
DIAMOND (Brandenburg, 2002);
Molecular graphics: SHELXL97 (Sheldrick, 2008); PLATON (Spek, 2003);
WinGX (Farrugia, 1999)

The results of these synthetic, spectral and structural studies are presented and
discussed in the thesis. The thesis is broadly divided into EIGHT CHAPTERS with
several sections in each chapter.

Chapter 1 gives an introduction to the spectroscopic techniques and an
overview of the subject of crystal structure studies, while Chapter 2 gives an
introduction to the chemistry of esters, overviews the chemistry of arylsulphonamides
and sketches the objectives and scope of the present work.

Chapter 3 describes the preparations, characterisations, infrared, \(^1\)H and \(^{13}\)C
NMR spectra of 54 aryl substituted benzoates of the type 2/3/4-halo/methyl-phenyl
2/3/4-chloro/methyl/methoxy benzoates, along with a review of literature on the
infrared and NMR spectral studies of benzoates. The C=O absorption frequencies of
the present aryl substituted benzoates have been compared with the reported aryl
benzoates and aryl para substituted benzoates and also with corresponding
benzanilides and substituted benzanilides. The variations of these absorption
frequencies with substitution in the aryl benzoates are also shown in terms of line
diagrams. The comparison showed that there are no particular trends in the variations
of these frequencies on substitution of either the electron withdrawing or donating
groups.

The chemical shifts of aromatic protons of the phenolic ring were calculated in
three different ways, while those of the benzyol ring were calculated in two ways. The
calculated chemical shifts of various aromatic protons of both the phenolic and
benzoyl rings by different methods have been compared with each other and with the
experimental values. The overall comparison of all the calculated and observed
chemical shifts of both the aromatic protons and carbons in all the aryl substituted
benzoates revealed that the different procedures of calculation lead to almost the same
values in most cases and are in reasonable agreement with the experimental chemical
shifts, indicating that the validity of the principle of additivity of the substituent
effects is quite good in these compounds. The variations of \(^{13}\)C=O and \(^{13}\)C-1 chemical
shifts of the above compounds with substitutions in both the phenolic and benzoyl rings of aryl substituted benzoates have also been shown in terms of line diagrams. These variations were too complex to generalize the trends.

**Chapter 4** describes the $^1$H and $^{13}$C NMR spectra of 15 N-(alkyl)substituted benzenesulphonamides and 36 N-(dichlorophenyl)/N-(dimethylphenyl)-2,4-disubstituted benzenesulphonamides in solution, along with a review of literature on the NMR spectra of aryl sulphonamides. It also compares and correlates the data. The $^1$H and $^{13}$C chemical shifts of the N-(alkyl)substituted benzenesulphonamides of the general formula, $4$-$XC_6H_4SO_2NHR$ were calculated in two different ways. The chemical shifts of the aromatic protons and carbons in the aniline phenyl ring of the compounds, $2,4-(CH_3)_2C_6H_4SO_2NH(i,j-X_2C_6H_5)$, $2$-$CH_3$-$4$-$ClC_6H_5SO_2NH(i,j-$X_2C_6H_5$), $2,4$-$Cl_2$-$C_6H_4SO_2NH(i,j-$X_2C_6H_5$) (where $i,j-X_2 = 2,3$-$Cl_2$, $2,4$-$Cl_2$, $2,5$-$Cl_2$, $2,6$-$Cl_2$, $3,4$-$Cl_2$, $3,5$-$Cl_2$, $2,3$-(CH$_3)_2$, $2,4$-(CH$_3)_2$, $2,5$-(CH$_3)_2$, $2,6$-(CH$_3)_2$, $3,4$-(CH$_3)_2$ or $3,5$-(CH$_3)$) were calculated in three ways, while those of sulphonyl ring were calculated in two ways. The calculated chemical shifts by the different methods are compared well with the observed values.

**Chapter 5** describes the crystal structures of phenyl, monosubstitutedphenyl and disubstitutedphenyl benzoates, along with a review of crystal structure studies on esters. Comparison of the crystal data revealed that the crystal system and the space group of the phenyl benzoate changes with monosubstitution. But they get restored to monoclinic crystal system on introducing the second substitutent. Mean C-C ring distances are little affected on substitution in the phenolic ring. The electron withdrawing substituents generally decreased the C(1)-O(1) bond length, while the electron donating substituents slightly increased them. The bond lengths O(1)-C(7), C(7)-O(2) and C(7)-C(8) were little affected by substitution and the effect did not follow a trend. Generally, the C(2)-C(1)-C(6) bond angle was not much affected by substitution, except on 2,3 and 2,6-disubstitutions. The variation of other bond angles does not follow any trend, although in some cases 2,6-disubstitution has marked effect. The torsional angles C(1)-O(1)-C(7)-C(8) and C(1)-O(1)-C(7)-O(2) are affected only on meta substitution and 2,3-disubstitution. We do not have the data on ortho substitution. They are likely to affect these angles. The next three angles also
changed on substitution. The dihedral angles are considerably affected on meta and disubstitution.

Chapter 6 describes the crystal structures of monosubstituted phenyl 4-methylbenzoates, dichlorophenyl 4-methylbenzoates and 4-chlorophenyl/4-methylphenyl 4-chlorobenzoates. The effect of substitution on the crystal geometry could not be considered as the data for the unsubstituted phenolic ring was not available and our effort to get single crystals of the compound was not successful.

Chapter 7 describes the crystal structures of 3,4-dichlorobenzene-sulphonamide, 4,6-dimethylbenzene-1,3-disulphonamide and potassium 4-chlorobenzenesulphonate along with a review of literature on crystal structure studies on aryl sulphonamides. The comparison of the crystal structure data of the parent and the substituted benzenesulphonamides revealed that the crystal system remains the same with all the substituents except with the mixed substitution. Only the space group changed on substitution. The substituents in the phenyl ring increased the S-O and C-S bond lengths. The effect of substitution on the \( C_{\text{ring}} - C_{\text{ring}} \) mean distances was minimal and on the bond angles it was non-uniform.

Chapter 8 describes the crystal structures of two monosubstituted benzenesulphonamides and three disubstituted benzenesulphonamides, along with a review of crystal structure studies on aryl sulphonamides. Effect of substitution on the bond lengths and angles was non-uniform.