SUMMARY
Organochalcogen compounds have long proved as valuable intermediate products in organic synthesis and convenient models for studying fundamental problems of theoretical chemistry in addition to exceptionally important substances from the practical viewpoint.

The present work is primarily focussed on the synthesis, characterization and evaluation of some new and hitherto unknown pyrimidyl and quinolinyl chalcogen compounds. The thesis has been apportioned into five chapters.

Chapter-1 instigate into the importance of chalcogens and organochalcogen compounds in different fields of science. The literature emphasizing on the synthesis and special applications of organosulfur, -selenium and -tellurium compounds has been extensively reported. The aim behind the present work, the objectives for the exploration of pyrimidyl and quinolinyl chalcogen chemistry has been also discussed.

Chapter-2 describes the experimental methods and techniques employed for the synthesis of novel pyrimidyl and quinolinyl chalcogen compounds. The methodologies have been suitably modified from the reported literature methods to achieve the targeted synthesis. The identity of compounds synthesized during the course of these investigations has been established with the help of elemental analysis and different spectroscopic techniques. The physical and analytical data along with the percentage yield of the product obtained using different methodologies have also been included.

Chapter-3 deals with the synthesis and characterization of novel pyrimidyl-sulfur, -selenium and -tellurium compounds. The chapter has been divided into eight sections.

Section-3.1 deals with the preparation of dipyrimidyl dichalcogenide compounds by using halopyrimidine structures as synthetic scaffolds. In particular, compounds 2-chloro-4,6-dimethylpyrimidine, 2,4-dichloropyrimidine and 2-chloro-4-methoxypryimidine were selected as the starting materials for the targeted pyrimidyl chalcogen compounds.

The synthetic strategy to prepare pyrimidyl chalcogen compounds employed 100% hydrazine hydrate in DMF to reduce chalcogens to generate dichalcogenide anions $E_2^2$ (E = S, Se, Te) followed by reaction with chloropyrimidines to give the dichalcogenide compounds in good yield. Alkaline hydrazine hydrate employed as the
reducing reagent for the chalcogens was easily accessible, low in cost and leads to clean reactions. This reagent was also realized to be selective in terms of exclusive generation of dichalcogenide ions (Scheme 1).

\[
4E + N_2H_4.H_2O + 4NaOH \xrightarrow{DMF} 2Na_2E_2 + 5H_2O + N_2
\]

**Scheme 1.** Reaction scheme showing the synthesis of bis(4,6-dimethyl-2-pyrimidyl) dichalcogenide/bis(4-dimethylamino-2-pyrimidyl) dichalcogenide and bis(4-methoxy-2-pyrimidyl) dichalcogenide compounds

The preparation of bis(4-dimethylamino-2-pyrimidyl) dichalcogenide compounds involved reduction of chalcogen atom to dichalcogenide anion by hydrazine hydrate in alkaline medium followed by relatively fast nucleophilic substitution reaction on C-2 of 2,4-dichloropyrimidine (a position w.r.t both nitrogen in the ring). The advantage of this methodology is the selective nucleophilic substitution of chlorine atom at second position of 2,4-dichloropyrimidine by dichalcogenide anion. An interesting observation in this reaction is the simultaneous substitution of chlorine atom at fourth position of 2,4-dichloropyrimidine by dimethylamino group from the solvent dimethylformamide. It is well known that DMF can act as formylating agent, however, in these reactions it acts as nucleophilic reagent leading to replacement of activated chloro group by dimethylamino
group, \(-\text{N(CH}_3\text{)}_2\) (Scheme 2). The dimethylamino group being more bulky and less nucleophilic than the dichalcogenide anion attacks the fourth position of the pyrimidine ring.

\[
\begin{align*}
\text{OH}^- + \text{H-C-N(CH}_3\text{)}_2\text{CH}_3 & \rightarrow \text{N(CH}_3\text{)}_2\text{CH}_3 + \text{H-OH} \\
\text{H}_3\text{C}^- + \text{[C-Cl-N]} & \rightarrow \text{[C-Cl-NMe}_2\text{]}^{-} & \rightarrow & \text{[NMe}_2\text{]}_2
\end{align*}
\]

**Scheme 2.** Mechanism showing the synthesis of bis(4-dimethylamino-2-pyrimidyl) dichalcogenide compounds

In a series of reactions, nucleophilic substitution of the chloro group at the C-2 position of the pyrimidine ring was selectively achieved i.e., with the retainment of the C-4 chloro group by generating the dichalcogenide anion \(E_2^-\) \((E=S, \text{Se}, \text{Te})\) in ethanol from elemental chalcogen using sodium borohydride as the reducing reagent. Bis(4-chloro-2-pyrimidyl) dichalcogenide and bis(2-pyrimidyl) disulfide/diselenide compounds were prepared by employing 2,4-dichloropyrimidine and 2-chloropyrimidine as the starting materials (Scheme 3 and Scheme 4).

\[
\begin{align*}
E_2^- & + \text{X-[N-Cl]} \rightarrow \text{[X-N]} & E & = S, \text{Se}, \text{Te}
\end{align*}
\]

**Scheme 3.** Reaction scheme showing the synthesis of bis(4-chloro-2-pyrimidyl) dichalcogenide and bis(2-pyrimidyl) disulfide/diselenide compounds.
Attempts were made to selectively substitute the chlorine at C-4 of 2,4-dichloropyrimidine to prepare bis(2-chloro-4-pyrimidyl) dichalcogenide (Scheme 5) by converting the corresponding halogenopyrimidine to pyrimidyl magnesium chloride at room temperature in THF by treatment with \( \text{^1} \text{PrMgCl} \) followed by its reaction with elemental chalcogen coupled with aerial oxidation. However, no product was isolated in this reaction.

**Scheme 5.** Reaction scheme for the attempted synthesis of bis(2-chloro-4-pyrimidyl) dichalcogenide.

Section 3.2 compiles the spectroscopic characterization of the prepared dipyrimidyl dichalcogenide compounds. Some of these compounds were obtained as crystalline solids, whose molecular structure has been determined through X-ray crystallographic analysis. Single crystals of bis(4,6-dimethyl-2-pyrimidyl) diselenide (Fig. 1), bis(4-dimethylamino-2-pyrimidyl) diselenide (Fig. 2), bis(4-dimethylamino-2-pyrimidyl) ditelluride (Fig. 3) and bis(4-methoxy-2-pyrimidyl) diselenide (Fig. 4) have been grown and analysed by X-ray diffraction.
Fig. 1. Bis(4,6-dimethyl-2-pyrimidyl) diselenide
Monoclinic, \( P_2_1/n \), \( a = 8.018(5) \) Å, \( b = 8.716(5) \) Å, \( c = 9.939(5) \) Å

Fig. 2. Bis(4-dimethylamino-2-pyrimidyl) diselenide
Monoclinic, \( C_2/c \), \( a = 9.236(11) \) Å, \( b = 13.217(15) \) Å, \( c = 12.739(16) \) Å

Fig. 3. Bis(4-dimethylamino-2-pyrimidyl) ditelluride
Monoclinic, \( C_2/c \), \( a = 9.515(5) \) Å, \( b = 13.576(5) \) Å, \( c = 12.372(5) \) Å

Fig. 4. Bis(4-methoxy-2-pyrimidyl) diselenide
Monoclinic, \( I_2/a \), \( a = 15.029(5) \) Å, \( b = 4.604(4) \) Å, \( c = 19.911(5) \) Å
Synthesis of unsymmetrical aryl/heteroaryl pyrimidyl chalcogen (E = S, Se, Te) compounds has been described in Section 3.3. The synthesized compounds include 4,6-dimethyl-2-(aryl selanyl) pyrimidine (Scheme 6), 4-chloro-2-(aryl chalcogeno) pyrimidine (Scheme 7) and alkylselanyl pyrimidine compounds (Scheme 8). All the reactions reported in this section make use of sodium borohydride to cleave either the E-E bond of several diaryl dichalcogenide compound or to synthesise alkyl selenols.

Scheme 6. Reaction scheme for the synthesis of 4,6-dimethyl-2-(aryl selanyl) pyrimidine compounds.

Scheme 7. Reaction scheme for the synthesis of some unsymmetrical pyrimidyl chalcogen (E = S, Se, Te) compounds.
Summary

\[ 3\text{Se} + 2\text{NaBH}_4 \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{NaHSe} + 2 \text{Br(OC}_2\text{H}_5)_3 + \text{H}_2\text{Se} + 5\text{H}_2 \]

\[ \text{NaHSe} + \text{RX} \rightarrow \text{RSeNa} + \text{HX} \]

\[ \text{RSeNa} + \text{SeR} \]

R = CH₃, C₂H₅, C₃H₅

Scheme 8. Mechanism for the synthesis of unsymmetrical chalcogen compounds.

The monochalcogen pyrimidyl compounds have been thoroughly characterized by different spectroscopic techniques viz., NMR (¹H, ¹³C, ⁷⁷Se), IR spectroscopy and mass spectrometry (Section 3.4.). The single crystal of the compound 4,6-dimethyl-2-(phenylselanyl) pyrimidine has been grown and analyzed (Fig. 5). The selective C-2 substitution reactions yielding 4-chloropyrimidyl compounds has been confirmed with the help of X-ray crystallographic analysis of two of the compounds in the series i.e., 4-chloro-2-(phenylselanyl) pyrimidine (Fig. 6) and 2-(p-tolylselanyl)-4-chloropyrimidine (Fig. 7).

Fig. 5. 4,6-Dimethyl-2-(phenylselanyl) pyrimidine
Monoclinic, P2₁/n, \(a = 8.290(12) \text{ Å}, b = 9.344(3) \text{ Å}, c = 15.234(5) \text{ Å}\)

Fig. 6. 4-Chloro-2-(phenylselanyl) pyrimidine
Monoclinic, P2₁/a, \(a = 13.399(14) \text{ Å}, b = 5.425(9) \text{ Å}, c = 14.620(9) \text{ Å}\)
Summary

Fig. 7. 2-(p-tolylselenyl)-4-chloropyrimidine
Monoclinic, P21/c, a = 8.947(4) Å, b = 11.997(6) Å, c = 10.791(6) Å

Synthesis and characterization of 2,4-bis(arylchalcogenyl)pyrimidine and 2-chloro-4,6-(chalcogenoaryl) pyrimidine compounds has been reported in Section 3.5 and Section 3.6. In this approach, sodium borohydride was used effectively for the cleavage of the E-E bond in diaryl dichalcogenide compounds as shown in Scheme 9.

Scheme 9. Reaction scheme for the synthesis of 2,4-bis(chalcogenoaryl) pyrimidine and 2-chloro-4,6-bis(arylchalcogenyl) pyrimidine compounds.
To throw more light on the structure and geometry of these molecules, single crystals of some representative compounds viz., 2-chloro-4,6-bis(naphthalen-1-ylselanyl) pyrimidine (Fig. 8), 2,4-bis(phenyltelluro) pyrimidine (Fig. 9), 2-chloro-4,6-bis(phenylselanyl) pyrimidine (Fig. 10) and 4,6-bis(p-tolylselanyl)-2-chloropyrimidine (Fig. 11) were studied by X-ray structural analysis.

Fig. 8. 2-Chloro-4,6-bis(naphthalen-1-ylselanyl) pyrimidine
Monoclinic, P-1, \( a = 9.703(4) \ \text{Å}, \ b = 10.223(5) \ \text{Å}, \ c = 11.168(5) \ \text{Å} \)

Fig. 9. 2,4-Bis(phenyltelluro) pyrimidine
Triclinic, P-1, \( a = 7.970(5) \ \text{Å}, \ b = 10.408(5) \ \text{Å}, \ c = 10.763(5) \ \text{Å} \)

Fig. 10. 2-Chloro-4,6-bis(phenylselanyl) pyrimidine
Orthorhombic, P212121, \( a = 8.711(5) \ \text{Å}, \ b = 9.410(5) \ \text{Å}, \ c = 18.888(5) \ \text{Å} \)

Fig. 11. 4,6-Bis(p-tolylselanyl)-2-chloropyrimidine
Orthorhombic, C 2 2 21, \( a = 8.786(5) \ \text{Å}, \ b = 13.571(5) \ \text{Å}, \ c = 15.244(5) \ \text{Å} \)
An attempt to explore the chemistry of the dipyrimidyl dichalcogenide compounds, the preparation of their organomercurial derivatives was tried and the synthesis of mercury 4-dimethylamino-2-pyrimidyl selenolate was successfully achieved (Section 3.7.).

**Scheme 10.** Reaction scheme for the synthesis of mercury 4-dimethylamino-2-pyrimidyl selenolate.

A study of the decomposition behaviour of unsymmetrical arylpyrimidyl selenide was done during the halogenation and oxidation reactions (Section 3.8.). However, the desired pyrimidyl arylselenenyl halides could not be isolated (Scheme 11). Instead, it resulted in the scission of C-Se bond and pyrimidyl halide was the major isolable product (Scheme 12). The entire reaction scheme can serve as a complimentary method for the conversion of selenides to corresponding pyrimidyl halides.

**Scheme 11.** Reaction scheme for halogenation of aryl pyrimidyl selenides.

\[ \text{Ar} = \text{C}_6\text{H}_5, \text{p-CH}_3\text{C}_6\text{H}_5, \text{C}_10\text{H}_7 \]

\[ X = \text{Cl, Br} \]
Summary

Scheme 12. Reaction scheme for synthesis of diaryl diselenides through halogenation.

Also during the preparation of selenoxide of 4-chloro-2-(phenylselanyl) pyrimidine, the reaction proceeded towards the scission of pyrimidyl carbon and selenium bond resulting in the formation of diphenyl diselenide and 2,4-dichloropyrimidine (Scheme 13).

Scheme 13. Reaction scheme for oxidation reaction of 4-chloro-2-(phenylselanyl) pyrimidine

Chapter 4 deals with the synthesis and characterization of novel quinolinyl-sulfur, -selenium and -tellurium compounds. The chemistry of quinolinyl chalcogen compounds compared to the phenyl and the pyridyl chalcogen compounds remains relatively unexplored. The present chapter is devoted to the synthesis of some new symmetrical and
unsymmetrical quinolinyl chalcogenide compounds by adopting a simple and less time consuming methodology.

The starting reagents for the synthesis of dichalcenolo[3,4-b] quinoline and 1,2-bis((2-chloroquinolin-3-yl)methyl) dichalcogenide, were prepared using Vilsmeier cyclisation. The most important step in the synthesis of these compounds was the preparation of oxygen sensitive sodium hydrogen chalcogenide, NaHE at ambient temperature for the nucleophilic substitution reactions of 2-chloro-3-formyl quinolines (Scheme 14). The solvent employed in the reaction was polar ethanol and the catalyst used was piperidine hydrochloride.

\[
\begin{align*}
\text{R} & \quad \text{CHO} & + \quad \text{NaHE} & \quad \text{Piperidine hydrochloride} & \quad \text{C}_2\text{H}_5\text{OH} & \quad \text{3H\{1,2\}dichalcenolo[3,4-b] quinoline(II)} \\
\text{1 (a-c)} & & & & & \\
\text{(a) R = OCH}_3; \text{ E = S, Se} & & & & & \\
\text{(b) R = H; E = S, Se} & & & & & \\
\text{(c) R = CH}_3; \text{ E = S, Se, Te} & & & & & \\
\text{1,2-bis(2-chloroquinolin-3-yl)methyl dichalcogenide(III)}
\end{align*}
\]

Scheme 14. Reaction scheme for synthesis of quinoline chalcogen compounds

A viable mechanism for the unusual ring closure involved in the reaction has been demonstrated in Scheme 15. In this sequence, the initial reaction involves the formation of an amine-aldehyde adduct such as hemiaminal or aminal 1 or 2. Nucleophilic displacement by the hydrogen chalcogenide anion on 1 or 2 followed by an intramolecular elimination leads to a short lived chalcenoaldehyde intermediate 3. In this reaction sequence, two displacement steps, each of which is separately well documented: oxygen is displaced by nitrogen, and nitrogen, in turn, by chalcogen have been proposed. Furthermore, we propose that the reduction of this chalcenoaldehyde 3 involves initial chalcogenophilic attack by the hydrogen chalcogenide anion, forming the
dichalcogenol anion 4. This dichalcogenol anion then can undergo intramolecular nucleophilic displacement of chloride ion at second position, giving the cyclic dichalcogenide II or it can react with chalcogenoaldehyde to give the dichalcogenide III.

**Scheme 15.** Mechanistic pathway for quinolinyl chalcogen compounds.

Encouraged by the success of this method, the modification in the present methodology was attempted, by repeating the reaction under same conditions but without the catalyst. This reaction resulted in conversion of the formyl group into hydroxymethyl group and no selenium insertion took place (Scheme 16).
In order to explore selective nucleophilic substitution of the chloro group at C-2 position of the quinoline ring, 2,4-dichloroquinoline was selected as the starting material. The synthetic strategy to prepare quinolynyl chalcogen compounds from 2,4-dichloroquinolione employed 100% hydrazine hydrate in DMF to reduce chalcogens to dichalcogenide anions $E_2^2$ (E = S, Se) followed by reaction with 2,4-dichloroquinolione to give the dichalcogen compounds in good yield (Scheme 17).

$$4E + N_2H_4.H_2O + 4NaOH \xrightarrow{DMF} 2Na_2E_2 + 5H_2O + N_2$$

The open structure of 1,2-bis((2-chloroquinolin-3-yl)methyl) dichalcogenide and cyclic structure of dichalcogenolo[3,4-b] quinoline has been unambiguously confirmed with the help of X-ray crystallographic analysis of four of the compounds in the series i.e., 3H-[1,2]diselenolo[3,4-b] quinoline (Fig. 12) and 1,2-bis(2-chloroquinolin-3-yl) methyl) diselenide (Fig. 13) 6-methoxy-3H-[1,2]diselenolo[3,4-b] quinoline (Fig. 14) and 1,2-bis((2-chloro-6-methoxyquinolin-3-yl)methyl) diselenide (Fig. 15). A variety of short distance contacts were found to exist in the solid state of these molecules, adding new dimensions to their study.
Fig. 12. 3H-[1,2]diselenolo[3,4-b] quinoline
Monoclinic, \( \text{P}\_1\text{ 21/n}\_1 \), \( a = 6.062(5) \) Å, \( b = 7.370(5) \) Å, \( c = 20.581(5) \) Å

Fig. 13. 1,2-Bis((2-chloroquinolin-3-yl)methyl) diselenide
Triclinic, \( \text{P}-1 \), \( a = 8.962(5) \) Å, \( b = 10.286(5) \) Å, \( c = 11.067(5) \) Å

Fig. 14. 6-Methoxy-3H-[1,2]diselenolo[3,4-b] quinoline
Monoclinic, \( \text{P} 21/n \), \( a = 6.112(4) \) Å, \( b = 7.370(5) \) Å, \( c = 22.779(6) \) Å

Fig. 15. 1,2-Bis((2-chloro-6-methoxyquinolin-3-yl)methyl) diselenide
Triclinic, \( \text{P}-1 \), \( a = 10.118(5) \) Å, \( b = 10.444(5) \) Å, \( c = 10.621(5) \) Å

Also X-ray crystallographic studies of the compound (2-chloro-6-methylquinolin-3-yl) methanol have been studied (Fig. 16).
Chapter-5 deals with the physicochemical properties of the synthesized pyrimidyl selenium compounds. Microemulsions comprising of water/AOT/isooctane (ME-I) and water/AOT+LC/isooctane (ME-II) have been used for solubilizing organoselenides *viz.*, bis(4-dimethylamino-2-pyrimidyl) diselenide, $\text{C}_{12}\text{N}_6\text{H}_{26}\text{Se}_2$ and bis(4-chloro-2-pyrimidyl) diselenide, $\text{C}_8\text{N}_4\text{H}_4\text{Se}_2\text{Cl}_2$. The incorporation of dipyrimidyl diselenide in microemulsion significantly affects the solubilization and electric percolation phenomenon. ME-II serves as a better host for the assimilation of dipyrimidyl diselenide as compared to ME-I.

The better behavior of ME-II further provides a gateway for synthesis of (4-chloro-2-(naphthalen-2-ylselanyl) pyrimidine and 2,4-bis(phenylselanyl) pyrimidine. Reaction mechanisms have been proposed in Scheme 18 and Scheme 19.

The novel compounds synthesized in microemulsion media was characterized using various spectroscopic techniques. The solid state structure of 2,4-bis(phenylselanyl)pyrimidine was established by single crystal X-ray crystallography (Fig.17).

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**Fig. 16. (2-Chloro-6-methylquinolin-3-yl) methanol**
Monoclinic, P21/c, $a = 14.517$ Å, $b = 4.612$ Å, $c = 14.468$ Å

**Fig. 17. 2,4-Bis(phenylselanyl)pyrimidine**
Triclinic, P-1, $a = 7.817(5)$ Å, $b = 10.248(5)$ Å, $c = 10.557(5)$ Å
Scheme 18. Probable mechanism for the synthesis of 4-chloro-2-(naphthalen-2-ylselanyl) pyrimidine

Scheme 19. Probable mechanism for the synthesis of 2,4-bis(phenylselanyl) pyrimidine