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Preparation and characterization of symmetrical bis[4-chloro-2-pyrimidyl] dichalcogenide (S, Se, Te) and unsymmetrical 4-chloro-2-(arylchalcogenyl) pyrimidine: X-ray crystal structure of 4-chloro-2-(phenylselanyl) pyrimidine and 2-(*p*-tolylselanyl)-4-chloropyrimidine

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ABSTRACT

Synthesis of a novel class of multinucleate pyrimidine chalcogen (S/Se/Te) derivatives has been successfully attempted for the first time by the selective substitution of chlorine at the C-2 position of 2,4-dichloropyrimidine with nucleophilic dichalcogenide anion E_2^{2-} (E = S, Se, Te) to afford bis[4-chloro-2-pyrimidyl] dichalcogenide. The highly electrophilic nature of 2,4-dichloropyrimidine compared to aryl chlorides has been further exploited to prepare a variety of 4-chloro-2-(arylchalcogenyl) pyrimidine compounds by substituting the chlorine exclusively at the C-2 position of 2,4-dichloropyrimidine with a variety of chalcogen bearing aryl anions ArE^- (Ar = phenyl, 1-naphthyl, *p*-tolyl, 4,6-dimethyl-2-pyrimidyl, 2-pyridyl, 4-methyl-2-pyridyl). All the newly prepared symmetrical and unsymmetrical pyrimidyl chalcogen compounds have been thoroughly characterized with the help of various spectroscopic techniques *viz*., NMR (^1H, ^{13}C, ^{77}Se), FT-IR and mass spectrometry (in representative cases). The crystal structures of 4-chloro-2-(phenylselanyl) pyrimidine and 2-(*p*-tolylselanyl)-4-chloropyrimidine have been determined by X-ray crystallography.

1. Introduction

Over the last thirty years, many important organic transformations were efficiently achieved using organochalcogen intermediates [1–5] that find extensive application in many diversified areas, such as metallurgy, chemicals, electronic conductors, and so on. A majority of these compounds are no longer considered toxic and some of them are used as antioxidants, enzyme inhibitors, cytotoxic agents for tumor cells and immunomodulators [6–9]. Organochalcogen compounds containing E–E (E = S, Se, Te) bond display an extremely rich chemistry and are of particular interest since these can (a) act as electrophilic [10] and nucleophilic [11] reagents in organic reactions (b) they exert protective effects against reactive oxygen species in the body [12] (c) have applications in ligand chemistry [13,14] and in various metal organic chemical vapor deposition (MOCVD) processes as precursors for the formation of thin films [15,16].

A variety of methods for the preparation of symmetrical diorganyl chalcogenides, R_2E and diorganyl dichalcogenides R_2E_2 (E = S, Se, Te) are known. Invariably, these methods are based on the reaction of alkali metal chalcogenides/dichalcogenides with appropriate haloalkanes in an aqueous or non-aqueous medium. The only difference in the preparative procedure adopted by various chemists lies in the generation of the alkali metal chalcogenides/dichalcogenides. Alkali metal chalcogenides/dichalcogenides can be prepared in situ by reducing elemental chalcogens by a variety of reducing agents *viz*. $LiAlH_4$ [17], $R_4N^+BH_4^-$ [18], $LiEt_3BH$ [19], $HOCH_2SO_2Na$ [20], and Na/NH_3 [21]. In literature use of some metals like indium [22], lanthanum [23], samarium [24] and their salts [25] have also been reported to cleave chalcogen–chalcogen bond. A number of alkyl/aryl selenides have been prepared by the direct nickel (II) [26] and copper (II)-catalyzed [27,28] coupling of selenide anions with aryl iodides. Different synthetic procedures for the preparation of the pyridyl selenium and tellurium compounds are also documented in the literature. Jerchel et al. [29] were the first to synthesize bis(4-pyridyl) diselenide and bis(4-pyridyl) selenide by reacting N-pyridyl (4-pyridinium) chloride with hydrogen selenide. Tanji et al. [30] reported the formation of alkyl pyridyl telluride by reacting bromopyridine with lithium alkyltellurolate. Recently, Bhasin and Singh

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[31] prepared various methyl-substituted bis(2-pyridyl) dichalcogenides (Se, Te) by using hydrazine hydrate as a reducing agent in basic medium using DMF as a solvent. Compared to the chemistry of pyridylchalcogen compounds, synthesis of pyrimidyl chalcogen moieties has not received much attention although the importance of compounds having a pyrimidine nucleus has been well documented in literature as anti-inflamatory [32], antitumor [33] agents etc. 5-Alkyl- or 5-alkylaryl-substituted pyrimidine derivatives are useful intermediates in the synthesis of antiviral nucleosides. Schinazi et al. [34] reported the synthesis and the biological activity of several 5-(phenylselenenyl)-pyrimidine nucleosides as potential antimicrobial agents. A variety of newly synthesized 6-phenylselenenyl acyclic pyrimidines [35,36] have recently been found to have potent anti-human immunodeficiency- virus-type-1 (HIV-1) activity. Bardos et al. [37] have synthesized successfully 5-selenium-substituted derivatives of uracil, 2′-deoxyuridine, and 2′-deoxyuridylic acid. Curiously, no attempt has been made to synthesize and characterize bis[4-chloro-2-pyrimidyl] dichalcogenide and 4-chloro-2-(arylchalcogenyl) pyrimidine compounds so, we wish to report herein a convenient method for preparation of hitherto unknown titled pyrimidyl chalcogen compounds.

2. Materials and methods

All experiments were carried out in dry oxygen–free nitrogen atmosphere. Sodium borohydride (Loba, purity > 99.5%), elemental selenium (Hi-media, purity > 99%), elemental sulfur (Hi-media, purity > 99%), elemental tellurium (Hi-media, purity > 99.5%) and uracil (Hi-media, purity > 95%) were newly purchased and stored in dessicator prior to use. 2,4-Dichloropyrimidine [38], diphenyl diselenide [39], diphenyl ditelluride [40], dinaphthyl diselenide [41], dipyridyl diselenide [31] and dipicolyl diselenide [31] were prepared by reported methods. IR spectra were recorded between KBr plates on a Perkin–Elmer Model 1430 ratio recording spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in CCl_4/$CDCl_3$ using tetramethylsilane as an internal standard and ^{77}Se with dimethylselenide as an external reference on a Jeol 300 MHz spectrometer. The mass spectra were obtained on Q-TOF micro mass spectrometer. Carbon, Hydrogen and Nitrogen were estimated micro analytically on a Perkin–Elmer 2400 CHN Elemental analyzer.

2.1. Synthesis of bis[4-chloro-2-pyrimidyl] dichalcogenide

To a vigorously stirred mixture of elemental chalcogen (S/Se/Te 75 mmol) and ethanol (30 ml), sodium borohydride (1.85 g, 50 mmol) was added slowly at 0 °C. The mixture was stirred for nearly 6 h at room temperature during which time the reduction was complete as indicated by the complete consumption of the chalcogen. The reduction of chalcogen is indicated by the color change of the reaction mixture i.e. deep red color in the case of selenium, brown color in the case of sulfur and purple color in the case of tellurium. A solution of 2,4-dichloropyrimidine (14.9 g, 100 mmol) dissolved in 15 ml ethanol was added dropwise. And the reaction was monitored by TLC till completion. After the completion of reaction, it was diluted with about 250 ml of distilled water and extracted in dichloromethane (3 × 50 ml). The organic layer was collected and solvent evaporated to get the crude product in solid form. The product was further subjected to purification on a silica column using hexane–ethyl acetate as eluant (5:1).

2.1.1. Bis[4-chloro-2-pyrimidyl] disulfide **1a**

Yield: 68%, white solid. M.p. 82–85 °C. Rf (10% Et_2O/hexane) .43. IR (KBr): ν 2924, 1539, 1400, 1327, 787, 681, 623 cm^{-1} ^{1}H NMR (300 MHz, CCl_4/$CDCl_3$, 25° C): δ = 8.39–8.37 (d, J = 6.0 Hz, 1H), 7.64–7.62 (d, J = 6.0 Hz, 1H) ppm. ^{13}C NMR: δ = 164.7, 160.0, 149.0, 118.0. $C_8H_4N_4S_2Cl_2$: calcd. C 32.98, H 1.37, N 19.24; found C 33.10, H 1.78, N 19.68.

2.1.2. Bis[4-chloro-2-pyrimidyl] diselenide **1b**

Yield: 65%, red crystalline solid. M.p.88–92° C. Rf (10% Et_2O/hexane) .39. IR (KBr): ν 2924, 1538, 1401, 1323, 582 cm^{-1}. ^{1}H NMR (300 MHz, CCl_4/$CDCl_3$, 25 °C): δ = 8.30–8.28 (d, J = 6.0 Hz, 1H), 7.58–7.56 (d, J = 6.0 Hz, 1H) ppm. ^{13}C NMR: δ = 167.9, 161.1, 158.8, 118.7. MS-EI: m/e (%): 387 ([$C_8H_4N_4Cl_2Se_2$]$^+$, 18), 384 ([$C_8H_2N_4Cl_2Se_2$]$^+$, 10), 227 ([$C_8H_2N_4Cl_2$]$^+$, 50). $C_8H_4N_4Se_2Cl_2$; calcd. C 24.80, H 1.03, N 14.47; found: C 25.10, H 1.36, N 14.07.

2.1.3. Bis[4-chloro-2-pyrimidyl] ditelluride **1c**

Yield: 55%, black solid. M.p.104–106° C. Rf (10% Et_2O/hexane) .34. IR (KBr): ν 2923, 1535, 1397, 1319, 571 cm^{-1}. ^{1}H NMR (300 MHz, CCl4/CDCl3, 25° C): δ = 8.11–8.07 (d, J = 12.0 Hz, 1H), 7.84–7.80 (d, J = 12.0 Hz, 1H) ppm. ^{13}C NMR: δ = 165.2, 160.9, 158.2, 126.7. $C_8H_4N_4Te_2Cl_2$: calcd. C 19.87, H 0.828, N 11.59; found C 19.42, H 0.980, N 12.00.

2.2. General procedure for synthesis of unsymmetrical pyrimidyl chalcogenides

To a solution of Ar_2E_2 (E = Se, Ar = phenyl, 1-naphthyl, p-tolyl, 4,6-dimethyl-2-pyrimidyl, 2-pyridyl, 4-methyl-2-pyridyl, E = S, Te, Ar = phenyl, 5 mmol) in 50 ml of C_2H_5OH-DMF (3:2) was added $NaBH_4$ (0.44 g, 12 mmol) in parts with continuous stirring at 0–5 C and the mixture was stirred for nearly 1 h at room temperature till the reduction was complete as indicated by the formation of colorless solution. The arylchalcogenide anion thus prepared was then alkylated with 2,4-dichloropyrimidine (1.49 g, 10 mmol) dissolved in 15 ml of DMF. After completion of the reaction ethanol was evaporated off in vacuo and the residue was extracted with dichloromethane (20 × 3 ml). The combined extract was then washed with water, dried (Na_2SO_4) and evaporated to leave the crude product; which was purified by column chromatography over silica gel (hexane–ethyl acetate) to furnish pure product.

2.2.1. 4-Chloro-2-(phenylthio) pyrimidine **2a**

Yield: 85%, white crystalline solid. M.p.39–42° C. Rf (10% Et_2O/hexane) .40. IR (KBr): ν 2923, 2361, 1548, 1400, 1330, 1192, 691 cm^{-1}. ^{1}H NMR (300 MHz, CCl_4/$CDCl_3$, 25° C): δ = 8.06–8.04 (d, J = 6.0 Hz, 1H), 7.50–7.38 (m, 5H), 6.52–6.50 (d, J = 6.0 Hz, 1H) ppm. ^{13}C NMR: δ = 172.7, 171.6, 160.4, 157.4, 157.0, 126.9. $C_{10}H_7N_2SCl$: calcd. C 53.93, H 3.14, N 12.58; found C 53.47, H 3.38, N 12.08.

2.2.2. 4-Chloro-2-(phenylselanyl) pyrimidine **2b**

Yield: 75%, white crystalline solid. M.p.49–51° C. Rf (10% Et_2O/hexane) .37. IR (KBr): ν 2924, 1542, 1518, 1478, 1439, 790, 668, 592 cm^{-1}. ^{1}H NMR (300 MHz, CCl_4/$CDCl_3$, 25° C): δ = 8.08–8.06 (d, J = 6.0 Hz, 1H), 7.70–7.66 (d, J = 12.0 Hz, 2H) 7.52–7.41 (m, 3H), 6.71–6.69 (d, J = 6.0 Hz, 1H) ppm. ^{13}C NMR: δ = 162.6, 161.3, 160.8, 159.8, 157.2, 120.0. ^{77}Se NMR : δ = 500 ppm. MS-EI: m/e (%): 271.4 ([$C_{10}H_7N_2SeCl$+1]$^+$, 100), 269.4 ([$C_{10}H_7N_2SeCl$-1]$^+$, 8). $C_{10}H_7N_2SeCl$: calcd. C 44.36, H 2.58, N 10.35; found C 44.40, H 2.16, N 9.98.

2.2.3. 4-Chloro-2-(phenyltelluryl) pyrimidine **2c**

Yield: 64%, yellow crystalline solid. M.p.48–50° C. Rf (10% Et_2O/hexane) .34. IR (KBr): ν 2922, 1536, 1509, 1396, 1321, 661, 574 cm^{-1}. ^{1}H NMR(300 MHz, CCl_4/$CDCl_3$, 25° C): δ = 7.96–7.86 (m, 3H), 7.50–7.45 (d, J = 15.0 Hz, 1H), 7.43–7.33 (d, 2H), 6.85–6.80 (d, J = 15.0 Hz, 1H) ppm. ^{13}C NMR: δ = 165.4, 160.9, 156.3, 141.3, 130.4, 130.0, 124.8, 124.4, 112.3. MS-EI: m/e (%): 318.6 ([$C_{10}H_7N_2TeCl$]$^+$, 34.5), 231.8

($[C_4H_2N_2Te]^+$, 74), 190.9 ($[C_{10}H_7N_2Cl]^+$, 17). $C_{10}H_7N_2TeCl$: calcd. C 37.85, H 2.20, N 8.83; found C 37.76, H 2.39, N 8.79.

2.2.4. 2-(p-tolylselanyl)-4-chloropyrimidine ***2d***

Yield: 76%, light yellow crystalline solid. M.p.75–78° C. Rf (10% Et_2O/hexane) .36. IR (KBr): ν 2924, 1542, 1399, 1324, 1665, 834, 669 cm^{-1}. ^1H NMR(300 MHz, $CCl_4/CDCl_3$, 25° C): δ = 8.27–8.20 (d, J = 21.0 Hz, 1H), 7.73–7.68 (d, J = 15.0 Hz, 2H), 7.30–7.25 (d, J = 15.0 Hz, 2H), 6.81–6.74 (d, J = 21.0 Hz, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR: δ = 176.0, 160.6, 157.1, 140.5, 136.8, 131.9, 121.3, 119.2, 118.3, 117.5, 21.5. MS-EI: m/e (%): 284 ($[C_{11}H_9N_2SeCl]^+$, 100), 227 ($[C_8H_4N_4Cl_2]^+$, 8), 204 ($[C_{11}H_9N_2Cl]^+$, 41). $C_{11}H_9N_2SeCl$: calcd. C 46.39, H 3.16, N 9.84; found C 46.89, H 3.50, N 9.44.

2.2.5. 4-Chloro-2-(naphthalen-2-ylselanyl) pyrimidine ***2e***

Yield: 57%, yellow crystalline solid. M.p.104–108° C. Rf (10% Et_2O/hexane) .30. IR (KBr): ν 2925, 1541, 1399, 1324, 791, 669 cm^{-1}. ^1H NMR(300 MHz, $CCl_4/CDCl_3$, 25° C): δ = 8.27–8.22 (t, 1H), 8.03–7.99 (m, 2H), 7.91–7.87 (t, 2H), 7.62–7.44 (m, 3H), 6.34–6.33 (d, 1H) ppm. ^{13}C NMR: δ = 175.0, 160.6, 157.2, 137.4, 134.5, 134.4, 131.9, 128.9, 128.1, 127.7, 126.2, 124.3, 118.73. ^{77}Se NMR: δ = 428 ppm. MS-EI: m/e (%): 320 ($[C_{14}H_9N_2SeCl]^+$, 15), 318.0 ($[C_{14}H_7N_2SeCl]^+$, 34), 316.0 ($[C_{14}H_5N_2SeCl]^+$, 13). $C_{14}H_9N_2SeCl$ calcd. C 52.41, H 2.80, N 8.73; found C 52.71, H 2.89, N 8.45.

2.2.6. 2-(4,6-Dimethylpyrimidin-2-ylselanyl)-4-chloropyrimidine ***2f***

Yield: 54%, white crystalline solid. M.p.148–149° C. Rf (10% Et_2O/hexane) .28. IR (KBr, cm^{-1}): ν 2925, 1581, 1543, 1398, 1328, 844, 640. ^1H NMR(300 MHz, $CCl_4/CDCl_3$, 25° C): δ = 8.36–8.34 (d, J = 6.0 Hz, 2H), 8.31–8.29 (d, J = 6.0 Hz, 2H), 6.79 (s, 1H), 2.39 (s, 6H) ppm. ^{13}C NMR: δ = 167.69, 157.33, 122.15, 118.23, 23.86. $C_{10}H_9N_4SeCl$: calcd. C 39.93, H 2.99, N 18.63; found: C 40.20, H 3.13, N 18.37.

2.2.7. 4-Chloro-2-(pyridin-2-ylselanyl) pyrimidine ***2g***

Yield: 65%, yellow powder. M.p.44–48 °C. Rf (10% Et_2O/hexane) .24. IR (KBr): ν 1542, 1449, 1401, 1323, 827, 670 cm^{-1}. ^1H NMR (300 MHz, $CCl_4/CDCl_3$, 25° C): δ = 8.58–8.56 (d, J = 6.0 Hz, 1H), 8.17–8.15 (d, J = 6.0 Hz, 1H), 7.69–7.61 (m, 2H), 7.33–7.29 (d, 1H), 7.27–7.24 (m, 1H) ppm. ^{13}C NMR: δ = 157.3, 150.9, 137.5, 130.3, 120.4, 120.3. MS-EI: m/e (%): 271 ($[C_9H_6N_3SeCl]^+$, 100), 236 ($[C_9H_6N_3Se]^+$, 10). $C_9H_6N_3SeCl$: calcd. C 39.85, H 2.21, N 15.49; found C 39.97, H 2.13, N 15.38.

2.2.8. 2-(4-Methylpyridin-2-ylselanyl)-4-chloropyrimidine ***2h***

Yield: 47%, yellow crystalline solid. M.p.55–57° C. Rf (10% Et_2O/hexane) 0.27. ^1H NMR(300 MHz, $CCl_4/CDCl_3$, 25° C): δ = 8.40–8.38 (d, J = 6.0 Hz, 1H), 7.64–7.61 (d, J = 9.0 Hz, 1H), 7.57–7.54 (d, J = 9.0 Hz, 1H), 7.37–7.35 (d, J = 6.0 Hz, 1H), 6.75–6.71 (t, 1H), 2.52 (s, 3H) ppm. $C_{10}H_8N_3SeCl$: calcd. C 42.10, H 2.80, N 14.73; found C 42.35, H 2.72, N 14.62.

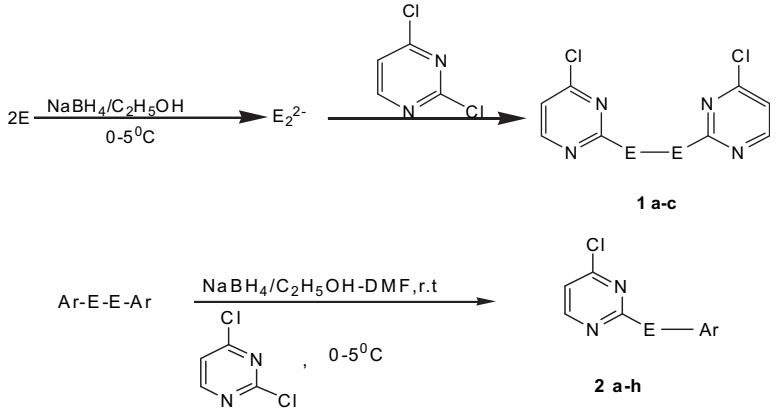
2.3. X-ray crystallographic studies

Diffraction quality single crystals of 4-chloro-2-(phenylselanyl) pyrimidine (**2b**) and 2-(*p*-tolylselanyl)-4-chloropyrimidine (**2d**) were obtained by the slow evaporation of dichloromethane–hexane solution of the corresponding compounds. Colorless crystals of (**2b**) and light yellow crystals of (**2d**) were obtained. Suitable crystals were chosen from a crop of crystals and mounted on glass fibers and data sets were collected on Nonius MACH3 diffractometer for the cell determination and intensity data collection. The diffraction data were collected using monochromatic Mo Kα radiation at 293(2) K and 150 (2) K for (**2b**) and (**2d**) respectively. The details of crystal structure determination and refinement parameters for (**2b**) and (**2d**) are given in Table 3 and Table 4 respectively.

Crystal structure was solved by direct methods (SHELXS-97) [42] and refined by full matrix least squares method.

3. Results and discussion

The research on the synthesis of the pyrimidine and its analogues has been going on continuously in search of new biologically active molecules. It is anticipated that pyrimidyl chalcogen compounds may also display the redox activity like other selenium derivatives of aniline, pyridine and quinoline. As a result of our ongoing project, we have reported an efficient synthetic route to bis(4-dimethylamino-2-pyrimidyl)dichalcogenides [43] (**1a**–**c**) by exploring the reaction of dichalcogenide anion E_2^{2-} in dimethylformaamide as the solvent. In this case, chlorine atom at C-2 position of 2,4-dichlropyrimidine is substituted by the in situ generated E_2^{2-} (E = S, Se, Te) anion. In addition, substitution at C-4 position by dimethylamino group is also facilitated by the dimethylformaamide used as a solvent. Thus, it was considered of interest to use another solvent i.e. absolute ethanol instead of DMF that would lead to retention of the chlorine at the C-4 position of 2,4-dichloropyrimidine. The reaction scheme for the

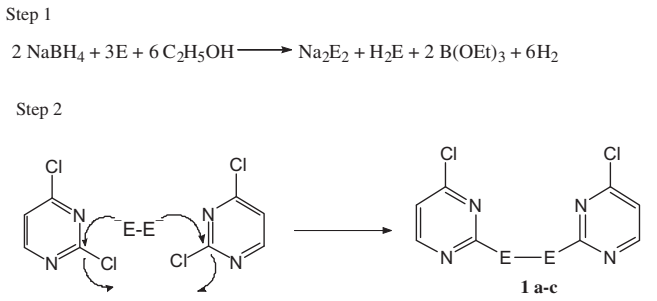


(**1 a-c**) E =S, Se, Te

(**2a**) E = S, Ar = C_6H_5, (**2 b, 2d-h**) E = Se, Ar = C_6H_5, p-$CH_3C_6H_5$, $C_{10}H_7$, $C_6N_2H_7$, C_5NH_4, C_6NH_6.

(**2c**) E = Te, Ar = C_6H_5

Scheme 1. Reaction scheme for the synthesis of some symmetrical and unsymmetrical pyrimidyl chalcogen (E = S, Se, Te) compounds.



Scheme 2. Mechanism for the synthesis of symmetrical chalcogen compounds (E = S, Se, Te) compounds.

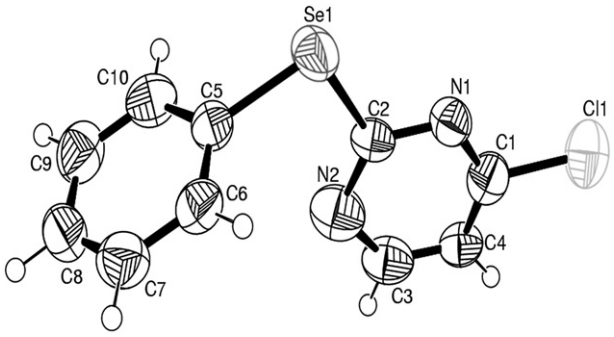


Fig. 1. ORTEP diagram showing the conformation and atom numbering scheme for 4-chloro-2-(phenylselanyl) pyrimidine (**2b**).

synthesis of the titled compounds uses sodium borohydride to carry out not only the reduction of elemental chalcogens but also for the reductive cleavage of chalcogen–chalcogen bond in diaryl dichalcogen compounds.

In order to solubilize completely the starting dichalcogen compounds as well as its nucleophilic borane complex, $[(ArE)B(OC_2H_5)_3]^-$, two volumes of DMF were added to three volumes of ethanol. Addition of DMF as a co-solvent improved the yield by solubilizing the diaryl chalcogenolate ion [44]. DMF being a highly polar solvent can be easily removed by simply washing with water. The entire scheme involving sodium borohydride as reducing agent was found effective for the synthesis of symmetrical and unsymmetrical pyrimidyl chalcogen compounds (**1a**–**c**, **2a**–**h**) (Scheme 1). The mechanism involved in the reaction is represented by Scheme 2 and Scheme 3. The advantage of this methodology to synthesize unsymmetrical chalcogen compounds is the selective nucleophilic substitution of chlorine atom at C-2 position of 2, 4-dichloropyrimidine by arylchalcogenide anion (ArE^-) resulting in the formation of C(Pym)-E bond.

The bis[4-chloro-2-pyrimidyl] dichalcogen compounds (**1a**–**c**) and 4-chloro-2-(arylchalcogenyl) pyrimidine (**2a**–**h**) thus prepared are stable enough to be purified by column chromatography (silica gel using hexane–ethyl acetate). The compounds are soluble in conventional organic solvents and have a long shelf life without any sign of decomposition even at room temperature.

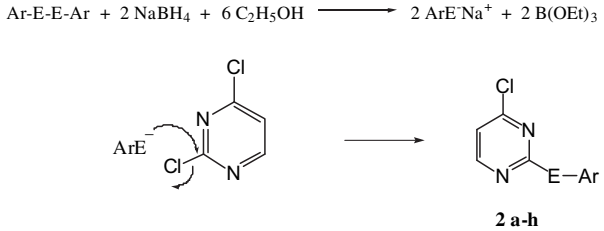
3.1. Spectroscopic studies

^{1}H NMR characterization of bis[4-chloro-2-pyrimidyl] dichalcogen compounds (**1a**–**c**) shows that the proton at C-5 of bis[4-chloro-2-pyrimidyl] ditelluride (**1c**) is shifted up field due to greater shielding of protons by tellurium metal as compared to selenium metal in bis[4-chloro-2-pyrimidyl] diselenide(**1b**). The resonance signals of pyrimidine ring in all of the unsymmetrical selenides show an up field shift for H-5 protons relative to those of the corresponding bis[4-chloro-2-pyrimidyl] diselenide(**1b**). Nevertheless, the signals appear up field with respect to the protons of 2,4-dichloropyrimidine. ^{13}C NMR spectra of bis[4-chloro-2-pyrimidyl] dichalcogen compounds (**1a**–**c**) display ^{13}C signal of the pyrimidyl group with values in the range of 118.0–167.0 (δ, ppm). The carbon signal of 4-chloro-2-(arylchalcogenyl) pyrimidine(**2a**–**h**) includes signals from both the pyrimidine ring as well as the aryl group. The mass spectra for 2-(*p*-tolylselanyl)-4-chloropyrimidine (**2d**) and 4-chloro-2-(pyridin-2-ylselanyl) pyrimidine (**2g**) show that the molecular ion peak is observed as base peak at *m*/*z* value 284 and 271 respectively. [M + 1] and [M − 1] peaks are observed for 4-chloro-2-(phenylselanyl) pyrimidine (**2b**). The fragment ions containing selenium show a highly characteristic and definite pattern of signal intensities depending on the natural abundance of various isotopes of selenium.

In IR spectra of these compounds, vibrations due to pyrimidyl and aryl groups can be easily identified. A strong and sharp band at 2900–2930 cm^{-1} has been assigned to aromatic C–H stretching and is consistent with the values found for C–H stretching vibrations in aromatic compounds. [45,46] An intense band around 1500–1550 cm^{-1} can be assigned to aromatic C=C stretching vibrations of the aryl rings, whereas a medium to sharp intensity band between 750 and 900 cm^{-1} has been assigned to ν_{C-H} deformation mode of aromatic ring. A comparison of ν_{E-C} (where E = S, Se, Te) stretching bands in pyrimidyl chalcogenides reveals a regular trend in the variation of ν_{E-C} absorption frequencies. In bis[4-chloro-2-pyrimidyl] dichalcogen compounds (**1a**–**c**) and 4-chloro-2-(arylchalcogenyl) pyrimidine (**2a**–**h**) a C–Cl band is observed near 620–700 cm^{-1}.

3.2. Solid-state structures: crystal structure determination of 4-chloro-2-(phenylselanyl) pyrimidine (*2b*) and 2-(p-tolylselanyl)-4-chloropyrimidine (*2d*)

To have an understanding of the structural details, single crystal X-ray diffraction of 4-chloro-2-(phenylselanyl) pyrimidine (**2b**) and 2-(*p*-tolylselanyl)-4-chloropyrimidine (**2d**) was carried out. A perspective view and atom numbering scheme of (**2b**) and (**2d**) are



(**2a**) E = S, Ar = C_6H_5, (**2 b, 2d-h**) E = Se, Ar = C_6H_5, p-$CH_3C_6H_5$, $C_{10}H_7$, $C_6N_2H_7$, C_5NH_4, C_6NH_6.
(**2c**) E = Te, Ar = C_6H_5

Scheme 3. Mechanism for the synthesis of unsymmetrical chalcogen compounds.

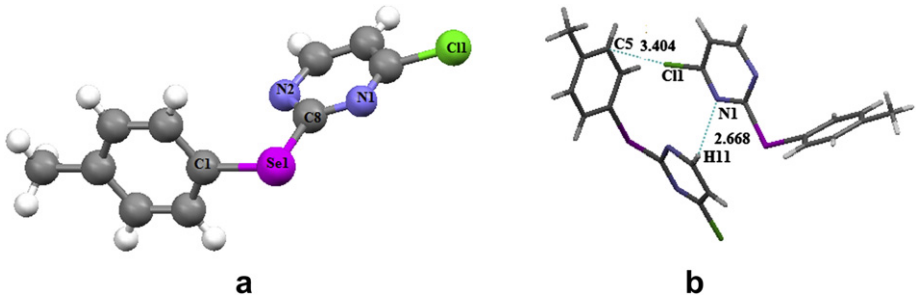


Fig. 2. (a) Diagram showing the conformation and atom numbering scheme (b) and the C···Cl and N···H interactions for 2-(*p*- tolylselanyl)-4-chloropyrimidine (**2d**).

Table 1
Selected bond parameters of (**2b**).

Bond length (Å)		Bond angle (°)	
Se(1)–C(2)	1.904(4)	C(2)–Se(1)–C(5)	99.88(15)
N(1)–C(1)	1.325(5)	C(4)–C(1)–N(1)	129.4(4)
C(9)–C(10)	1.359(6)	N(1)–C(1)–Cl(1)	114.0(3)
C(5)–C(10)	1.382(5)	C(6)–C(5)–Se(1)	119.4(3)
Torsion angles (°)			
C(2)–N(1)–C(1)–C(4)	0.3(6)		
C(3)–N(2)–C(2)–N(1)	−0.3(6)		
C(3)–N(2)–C(2)–Se(1)	−179.4(3)		
Se(1)–C(5)–C(10)–C(9)	179.7(3)		

given (Fig. 1 and Fig. 2 respectively). The important bond parameters for (**2b**) and (**2d**) are listed in Table 1 and Table 2 respectively.

The average C–C bond length in the pyrimidine ring in (**2b**) and (**2d**) is 1.304 Å and 1.329 Å respectively. The Se–C bond lengths in (**2b**) are [Se (1)–C (2), 1.904(4) Å], [Se (1)–C (5), 1.914(4) Å] and in (**2d**) are [Se (1)–C (1), 1.9157(19) Å] and [Se (1)–C (8), 1.9023(18) Å]. The average C–C bond length in phenyl ring in (**2b**) is 1.372 Å and in tolyl ring in (**2d**) is 1.390 Å. The observed bond angle C (2)–Se (1)–C (5) and C (2)–Se (1)–C (5) in (**2b**) and (**2d**) is 99.88(15) and 98.39(8) respectively. These bond angles indicate the distortion of sp^3 carbon from its regular tetrahedral geometry and established the 'V' shaped geometry about C–Se–C bond. Interestingly, the compound 2-(*p*-tolylselanyl)-4-chloropyrimidine (**2d**) has shown hydrogen-bonding interactions between the nitrogen atom of pyrimidyl ring of one crystal unit and hydrogen atom of the other pyrimidyl ring of other crystal unit. However, the compound 4-chloro-2-(phenylselanyl) pyrimidine (**2b**) displayed N–H intermolecular interactions between nitrogen of pyrimidyl ring and hydrogen of the phenyl ring within the crystal lattice. Also in 4-chloro-2-(phenylselanyl) pyrimidine (**2b**), short contacts are observed between C-3 of the pyrimidine ring and H-4 of the pyrimidine ring of the other molecule and another C···H interaction between C-4 of the pyrimidine ring and H-3 of the pyrimidine ring of the other molecule which is marked from the measured C···H distances which are less than the vander Waals distance (2.90 Å). Short contact is apparent between the carbon atom of tolyl ring C (6) and the chlorine attached to C (9) of the pyrimidyl group of the other molecule as indicated by distance (3.40 Å), which is shorter than the sum of their vander Waals radii (3.59 Å) in 2-(*p*-tolylselanyl)-4-chloropyrimidine (**2d**).

Table 2
Selected bond parameters of (**2d**).

Bond length (Å)		Bond angle (°)	
Se(1)–C(8)	1.9023(18)	C(8)–Se(1)–C(1)	98.39(8)
Se(1)–C(1)	1.9157(19)	N(1)–C(8)–N(2)	121.79(16)
N(1)–C(9)	1.325(2)	C(10)–C(9)–N(1)	129.14(18)
C(4)–C(7)	1.505 (3)	N(1)–C(9)–Cl(11)	115.42(14)
Cl(1)–C(10)	1.7390(19)	C(6)–C(1)–Se(1)	120.04(15)

Table 3
Crystal data and structure refinement for (**2b**).

Formula	$C_{10}H_7ClN_2Se$
Formula weight	269.59
Temperature/K	293(2) K
Crystal system	Monoclinic
Space group	*P*21/a
A/Å	13.3997(14)
B/Å	5.4254(9)
c/Å	14.620(9)
B/°	101.73(2)
Volume/$Å^3$	1174.5(5)
Z	4
Absorption coefficient/mm^{-1}	3.823
Density calc./mg/m^3	1.721
F(000)	528
2 theta/°	24.99
Index ranges	$-15 \le h \le 15, -6 \le k \le 5, -17 \le l \le 17$
Reflections collected	5605 [R(int) = 0.0251]
Reflections unique	1827
Parameters	127
GOOF	0.991
R_1/wR_2 [$I > 2\sigma(I)$]	0.0369/0.0973
R_1/wR_2 (all data)	0.0529/0.1013
largest res.Peak/e $Å^{-3}$	0.516

Table 4
Crystal data and structure refinement for (**2d**).

Formula	$C_{11}H_9ClN_2Se$
Formula weight	283.61
Temperature/K	150 (2) K
Space group	*P*21/c
a/Å	8.9473(4)
b/Å	11.9976(6)
c/Å	10.7913(6)
β/°	98.916(3)
Volume/$Å^3$	1144.41(10)
Z	4
Absorption coefficient/mm^{-1}	3.481
Density calc./mg/m^3	1.646
F(000)	560
2 theta/°	33.29
Index ranges	$-13 \le h \le 13, -17 \le k \le 17, -16 \le l \le 16$
Reflections collected	51,507 [R(int) 0.0312]
Reflections unique	4332
Parameters	137
GOOF	1.062
R_1/wR_2 [$I > 2\sigma(I)$]	0.0334/0.1011
R_1/wR_2 (all data)	0.0453/0.1078

4. Conclusion

The present report constitutes the first successful attempt to synthesize novel bis[4-chloro-2-pyrimidyl] dichalcogenide (S, Se, Te)and 4-chloro-2-(arylchalcogenyl) pyrimidine compounds by simple synthetic methodology. These compounds are anticipated to have potential applications in medicinal field.

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Appendix A. Supplementary material

CCDC 736021 and 736022 contain the supplementary crystallographic data for Compound **2b** and **2d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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