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SYNTHESIS AND CHARACTERIZATION OF SOME SYMMETRICAL SUBSTITUTED 1-(2-CHLOROETHYL)PYRAZOLE-BASED CHALCOGENIDES

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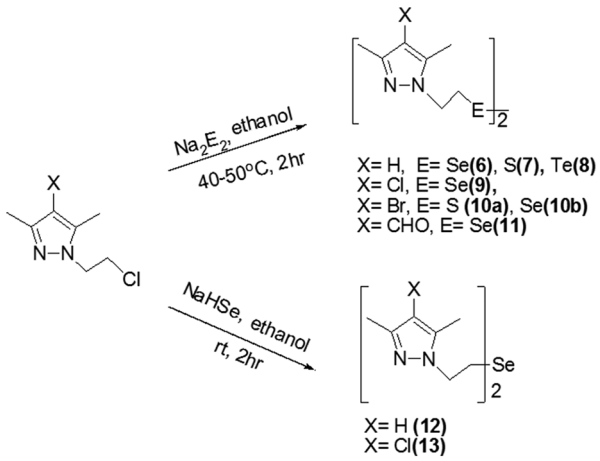
ABSTRACT The present paper describes the synthesis of some symmetrical substituted 1-(2-chloroethyl) pyrazole-based dichalcogenides and monochalcogenides by reacting different 3,4,5-trisubstituted 1-(2-chloroethyl) pyrazole derivatives with *in situ* prepared Na_2E_2 (E = S, Se, Te) and sodium hydrogen selenide, respectively. All compounds were fully characterized by different spectroscopic techniques, namely, IR, ^1H, ^{13}C, ^{77}Se nuclear magnetic resonance, and mass spectrometry. X-ray crystal structure determination of 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl)diselane (**10b**) reveals intermolecular Se·N·H interactions between two molecules.



KEYWORDS 3,5-Dimethylpyrazole, Organoselenium, Sodium borohydride, X-ray crystal structure.

INTRODUCTION

Organoselenium and organotellurium compounds are finding renewed interest as synthetic reagents in organic synthesis.[1,2] In addition to their synthetic applications, these compounds are gaining particular interest due to their significant applications in electronic industry,[3] as organic conductors[4] and precursors for semiconducting materials,[5] in biology,[6] and in medical imaging. In particular, organoselenium compounds have attracted attention since they find application in organic synthesis, materials synthesis, ligand chemistry, and biologically

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relevant processes.[7] It has long been known that many organoselenium compounds exhibit a variety of useful medicinal activities, including antibacterial, antifungal, antihypertensive, antioxidant, antiviral, antiparasitic, and antiradiation properties.[8] In addition, organoselenium compounds have proven useful as cancer chemopreventive[9] and Alzheimer's therapeutic agents.[10] It is worthy to note that the chemistry of alkyl, aryl, and mixed alkyl aryl chalcogenides has proliferated in the past decades and is of immense interest to organic chemists,[11] whereas the chemistry of pyrazolyl derivatives virtually remained unexplored, in spite of its greater utility. Recently, the chemistry of pyrazolyl derivatives has attracted the attention of scientist community due to their unique properties. The presence of nitrogen in the aromatic ring brings remarkable changes and has attracted considerable attention of the chemistry world as precursors in pharmacological compounds, for the preparation of liquid crystals, in the synthesis of polymers and as ligands in transition metal complexes. It is anticipated that the decoration of a pyrazole core with chalcogens may furnish molecules with pronounced or distinct biological activities. According to the above mentioned and the ongoing research interest in organochalcogen, it was decided to investigate whether any cooperativity might be gained by combining chalcogens to the pyrazole derivatives.

RESULTS AND DISCUSSION

Synthesis

3,5-Dimethylpyrazole (3,5-dmpz) is conveniently employed as a pyrazolato ligand and finds extensive use in the synthesis of various antibacterial N-1-substituted derivatives. In addition, it is used as an intermediate in the manufacture of organic dyestuffs. Synthesis of 3,5-dimethylpyrazole was carried out using acetylacetone and hydrazine hydrate in tetrahydrofuran as solvent.[12] N-alkylation of 3,5-dmpz was achieved by reacting it with 1,2-dichloroethane (DCE), a phase transfer catalyst tetrabromoammonium chloride (TBAC) in aqueous NaOH (Scheme 1).[13]

Reaction at the C-4 position of pyrazole occurs readily by an electrophilic substitution reaction. During present investigations, 4-halo derivatives of 3,5-dimethylpyrazole were synthesized in view of the important biological and pharmaceutical activities exhibited by substructures containing 4-halopyrazole.[14,15] A library of reagents has been well documented in the literature for the halogenation of C-4 position of pyrazole. However, reaction with N-chlorosuccinamide or N-bromosuccinamide in carbon tetrachloride has been employed in the present studies (**3a**, **3b**) (**Scheme 1**).[16] N-alkylation of the 4-halo-3,5-dimethylpyrazole was carried out by reacting it with DCE in aqueous NaOH in the presence of TBAC as a phase transfer catalyst and yellow oil in quantitative yield has been obtained (**4a**, **4b**) (**Scheme 1**).

The synthesis of 3,5-dimethyl pyrazole-4-carbaldehyde was carried out by the formylation of **2** at C-4 position by Vilsmeier Haack method to obtain N-chloroethyl-3,5-dimethylpyrazole-4-carbaldehyde (**5**) (**Scheme 1**).[17]

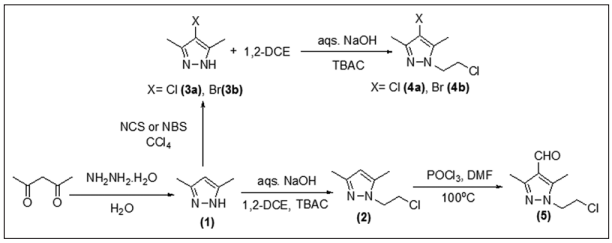
After the successful preparation of the starting precursors, an attempt was made to synthesize the desired chalcogenated derivatives of substituted 1-(2-chloroethyl)pyrazole by reacting the newly prepared precursors with the *in situ* prepared solution of sodium dichalcogenides, Na_2E_2 (E = S, Se, Te) in ethanol as described in **Scheme 2**. Sodium borohydride, being a cheap and readily available reducing agent, was employed to reduce elemental sulfur/selenium/tellurium. During the reaction, the temperature was maintained at 40-50°C for 2 h which afforded the corresponding substituted 1-(2-chloroethyl) pyrazole dichalcogenides in good yields. 1-(2-chloroethyl) pyrazole-derived monochalcogenides, in addition, were synthesized in good yield as solid compounds by reacting the above reactants with *in situ* prepared sodium hydrogen selenide (**12**, **13**). In this case, the reaction performed at room temperature for 2 h.

It is important to mention that all reactions were carried out under an inert atmosphere. Slow addition of reactants ensured improved yields. The compounds were light sensitive and changed color from yellow to red gradually over a period of time.

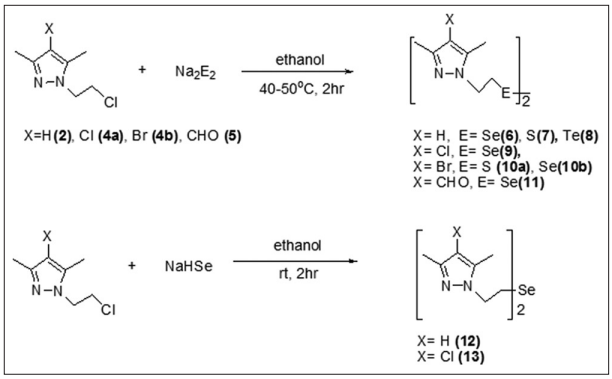
All compounds are soluble in common polar organic solvents, namely, chloroform, dichloromethane, and dimethylsulfoxide. The synthesized compounds were analytically pure and were fully characterized by different spectroscopic techniques, namely, FTIR, ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, mass spectroscopy, and ^{77}Se NMR and X-ray in some representative cases. Physical data of synthesized compounds are presented in **Table 1**.

Spectroscopic studies

In proton NMR spectra, peaks corresponding to two methylene groups (-CH_2Se or –CH_2S and –CH_2N) in all



Scheme 1: Synthesis of substituted pyrazole derivatives



Scheme 2: Synthesis of symmetrical substituted pyrazole-derived dichalcogenides/monochalcogenides

Table 1: Physical data of symmetrical substituted pyrazole dichalcogenides

Compounds	Physical state/color	Melting point (°C)	Yield (%)
1,2-*bis*(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane($C_{14}H_{22}N_4Se_2$)	Yellow solid	60-65	67
1,2-*bis*(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl) disulfane($C_{14}H_{22}N_4S_2$)	White solid	30-35	53
1,2-*bis*(2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane($C_{14}H_{20}N_4Se_2Cl_2$)	Red solid	56-60	75
1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane($C_{14}H_{20}N_4Se_2Br_2$)	Red solid	55-60	74
1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) disulfane($C_{14}H_{20}N_4S_2Br_2$)	White solid	30-33	63
1-(2-(2-(2-(4-Formyl-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselanyl) ethyl)-3,5-dimethyl-1H-pyrazole-4-carbaldehyde($C_{16}H_{22}O_2N_4Se_2$)	Red solid	60-65	76
1,2-*bis*(2-(3,5-dimethyl-1H-pyrazol-1-yl) ethyl)ditellane($C_{14}H_{22}N_4Te_2$)	Red viscous liquid	-	56
Bis(2-(3,5-dimethyl-1H-pyrazol-1-yl) ethyl)selane($C_{14}H_{22}N_4Se$)	Pale white solid	60-62	66
Bis(2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl) ethyl)selane($C_{14}H_{20}N_4$ $SeCl_2$)	White solid	63-65	57

3,4,5-trisubstituted 1-(2-chloroethyl) pyrazole-derived di/monochalcogenides appeared as triplets in the aliphatic region in the range of 4.323-2.899 (δ, ppm). An upfield shift in the peak values of methylene groups has been observed in all these compounds due to substitution of halide ion by a chalcogen atom. Two single peaks between 2.32 and 2.83 (δ, ppm) correspond to two methyl groups attached at C-3 and C-5 position of the pyrazole ring in these cases. A singlet appears at 9.87 (δ, ppm) for -CHO group in compound **11**. The ^{13}C NMR chemical shift for the pyrazole ring carbons appear in the range 104.89-185.87 (δ, ppm). The peaks corresponding to the methylene groups appeared between ~ 20 and 50 (δ, ppm). For compound **11,** signal at 184.29 (δ, ppm) appears for carbon of -CHO group. IR spectra give relevant peaks for C-Se bond in the region 400-500 cm^{-1}. Vibrations due to pyrazole ring could be easily identified due to presence of strong and sharp band around 1455-1600 cm^{-1} which could be assigned to aromatic C=C stretching vibrations of aryl rings. Absorption arising from C-H stretching in the alkanes occurs in region of 3000-2840 cm^{-1}. Ring stretching vibration occurs between 1600 and 1300 cm^{-1} for C=N of aromatic ring.

It is clear from the data presented in **Table 2** for ^{77}Se NMR spectra of representative compounds that the signals appeared more downfield in case of diselenides as compared to monoselenide.

Mass spectra of all the compounds show predominately signals due to $[M]^+$ and $[M+23]^+$. The molecular ion peak in the compound **11** appears at m/z 485 (100%) corresponding to $[C_{16}H_{22}N_4Se_2O_2]^+$ + 23 in addition to another peak appearing at m/z 231 (20%) corresponding to the fragment $[C_8H_{11}N_2SeO]^+$.

X-ray structure elucidation of 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl)diselane (10b)

Reddish brown-colored crystals of 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl)diselane were obtained using a chloroform–hexane (1:1,v/v) mixture with slow evaporation at room temperature. The ORTEP view of the compound has been presented in Figure 1. A crystal with approximate dimensions 0.230 × 0.180 × 0.150 mm^3 was selected under ambient conditions. The compound crystallizes in a triclinic

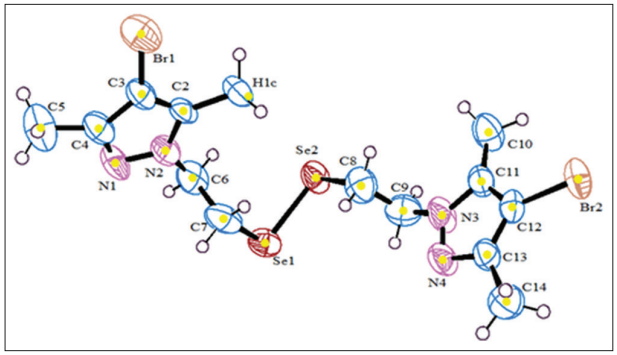


Figure 1: ORTEP diagram of 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl)diselane (10b)

crystal system with P-1 space group. The unit cell parameters were found to be a = 5.51158 (4) Å, b = 12.1040 (14) Å, c = 14.4468 (8) Å, α = 91.335 (7)°, β = 93.604 (5)°, and γ = 92.982 (7)° with unit volume, V = 960.96 (14) $Å^3$. Number of atoms per unit cell is 2. The structure was resolved by direct methods and refined by full-matrix least squares method using SHELX-2013 program package. The final cycle of full-matrix least squares refinement was based on 6290 observed reflections and 203 variable parameters for [I > 2σ(I)] converged with unweighted and weighted agreement factor of R_1 = 0.0519 and wR_2 = 0.1271 over a θ range of 3.253-24.997°. All non-hydrogen atoms were refined as anisotropic, the hydrogen atomic positions were constrained in an idealized geometry relative to the bond carbon, and isotropic thermal parameters were fixed.

The C-Se, C-Br, and Se-Se bond distances for the compound are tabulated in **Table 3**. The Se1-Se2 bond distance is 2.321(12) Å, whereas the C7-Se1 and C8-Se2 bond distances are 1.967(9) Å and 2.022(8) Å, respectively. C3-Br1 and C12-Br2 bond distances are 1.858(7) Å and 1.866(7) Å, respectively, as depicted in **Table 3**. It is observed that the C-Se and C-Br bond distances lie within the range of sum of the van der Waals radii. The C(7)-Se(1)-Se(2) and C(8)-Se(2)-Se(1) bond angles are 98.5(2)° and 101.4(3)°, respectively. The decrease in bond angles is attributed to the presence of two lone pairs on selenium atoms.

The torsional angles of the compound have also been tabulated in **Table 3**. It can be inferred from the values that Br2-C12-C11-C10 (0.50°) has a *syn* arrangement as the

torsional angle fall in the range between 0° and ±30°, whereas Se2-C8-C9-N3 (177.39°) and Br2-C12-C11-N3 (178.66°) have *trans* arrangement as the value falls in the range of 150° to ± 180°.

In the extended short contacts of the molecule, five prominent weak bonds have been identified giving rise to a complex arrangement of molecules as depicted from the **Figure 2**. Two molecules are showing interactions through Se1·N4 (3.140 Å) and N4 H7A (2.701 Å), whereas the third molecule is interacted by Br1·H8A (2.934 Å) weak bond. Moreover, two more interactions N1· Br2 (3.230 Å) and H5C·H10B (2.242 Å) as have been identified in the expanded fragment.

In the packing arrangement also (**Figure 3**), there are present two molecules each situated in such a manner that no intermolecular interactions are present between the two. However, the non-bonding interactions with the molecules situated outside the unit cell are observed as discussed earlier. Full details of the crystal structure determination and refinement parameters are depicted in **Table 4**.

EXPERIMENTAL

Materials and instrumentation

All chemicals were stored in dessicator before use and were newly purchased or synthesized. Starting materials were synthesized according to the reported methods. ^{1}H NMR and ^{13}C NMR were recorded at 400 MHz in $CDCl_3$ on Bruker 400 with TMS as an internal reference. ^{77}Se NMR spectra were recorded on the multiprobe NMR spectrometer using diphenyl diselenide (Ph_2Se_2) as an external reference. Infrared spectra were recorded in the range of 4000-200 cm^{-1} on a thermoscientific nicolet iS50 FT-IR. Mass spectrometry was carried out on ES-MS Q-TOF.

Table 2: ^{77}Se NMR data of representative compounds

Compounds	^{77}Se (δ, ppm)
1,2-*bis*(2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl) ethyl) diselane (**9**)	295.58
1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl) ethyl) diselane (**10b**)	294.53
1-(2-(2-(2-(4-Formyl-3,5-dimethyl-1H-pyrazol-1-yl) ethyl) diselanyl)ethyl)-3,5- dimethyl-1H -pyrazole-4-carbaldehyde (**11**)	295.82
Bis (2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl) ethyl) selane (**13**)	139.75

General procedure for the synthesis of substituted 1-(2-chloroethyl)pyrazole dichalcogenides

In a 100 ml, three necked flask fitted with condenser, was added ethanol (150 mL) and sulfur (1.2g, 38mmol)/ selenium (3.0g, 38mmol)/tellurium (4.9g, 38mmmol). To this solution was added sodium borohydride in portions at 0 degree C. After initial reaction had subsided, the reaction mixture was stirred to dissolve S/Se/Te element and expel any gas. The red (Na_2Se_2)/brown (Na_2S_2)/purple (Na_2Te_2) solution will be formed after half an hour. To this solution,

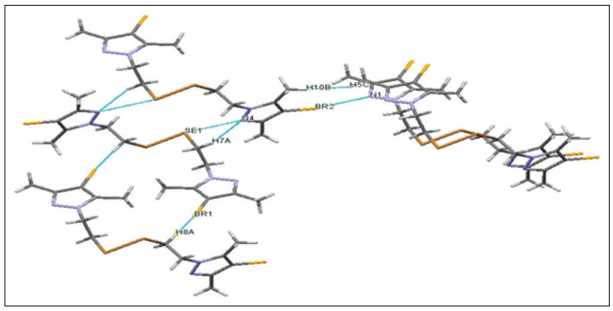


Figure 2: Two-dimensional array displaying short contacts Se1·N4 (3.140 Å), N4·H7A (2.701 Å), Br1·H8A (2.934 Å) and expanded contacts through N1·Br2 (3.230 Å) and H5C·H10B (2.242 Å)

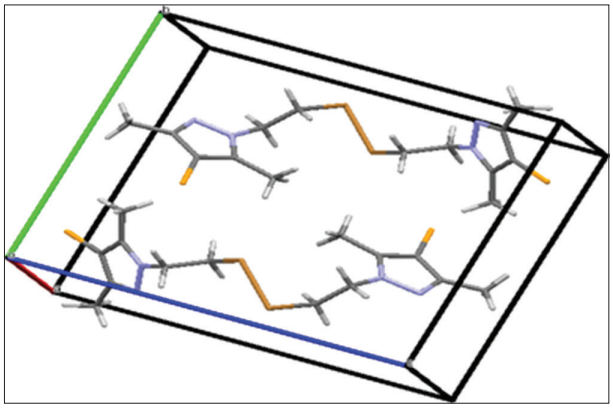


Figure 3: Crystal packing of 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl)diselane in a unit cell

Table 3: Important bond length and bond angles of 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane (10b)

Bond length (Å)		Bond angles (°)		Torsional angles (°)	
Se (1)-C (7)	1.967 (9)	C (7)-Se (1)-Se (2)	98.5 (2)	C8-Se2-Se1-C7	73.82
Se (1)-Se (2)	2.3218 (12)	C (8)-Se (2)-Se (1)	101.4 (3)	C9-C8-Se2-Se1	97.53
Se (2)-C (8)	2.022 (8)			C6-C7-Se1-Se2	71.95
Br (1)-C (3)	1.858 (7)			Se1-C7-C6-N2	-169.06
Br (2)-C (12)	1.866 (7)			Se2-C8-C9-N3	177.39
				Br2-C12-C11-N3	178.66
				Br2-C12-C11-C10	0.50

Table 4: Crystal data and structure refinement for 1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane (10b)

Compound	1,2-*bis*(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl)diselane
Empirical formula	$C_{14}H_{20}Br_2N_4Se_2$
Formula weight	562.08
Temperature	293 (2) K
Wavelength	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å)	a=5.51158 (4), b=12.1040 (14), c=14.4468 (8), α=91.335 (7)°, β=93.604 (5)°, γ=92.982 (7)°
Volume	960.96 (14) Å^3
Z	2
Density (calculated)	1.943 Mg/m^3
Absorption coefficient	8.007 mm^{-1}
F (000)	540
Crystal size	0.230×0.180×0.150 mm
Theta range for data collection	3.253-24.997°
Index ranges	-6<=h<=6, -14<=k<=14, -17<=l<=16
Reflections collected	6290
Independent reflections	3378 [R (int) = 0.0442]
Completeness of theta=24.997	99.6%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3378/0/203
Goodness of fit on F^2	1.037
Final R indices (I>2 sigma [I])	R_1=0.0519, wR_2=0.1271
R indices (all data)	R_1=0.0764, wR_2=0.1511
Extinction coefficient	n/a
Largest difference of peak and hole	0.695 and -0.764 e. Å^{-3}

suitable aryl alkyl halide (4.0 g, 25 mmol), dissolved in ethanol, was added with the help of a syringe. The reaction mixture was heated up to a temperature of 40-50°C and stirring continued for 2 h. The course of the reaction was monitored by TLC. After the completion of reaction, it was cooled to room temperature, extracted with diethyl ether. After removal of solvent, the crude product was further purified by column chromatography using hexane/ethyl acetate as eluent.

1,2-Bis(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl)diselane (6)

^{1}H NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 2.155 (*s*, 3H), 2.246 (*s*, 3H), 3.292-3.244 (*t*, J= 7.5Hz, 2H), 4.287-4.239 (*t*, J= 7.5Hz, 2H), 5.717 (*s*, 1H); ^{13}C NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 147.58, 138.66, 105.04, 49.06, 23.37, 13.54, 11.17; IR: *v* (cm^{-1}) 2968.7, 2936.23, 2861.41, 1548.04, 1456.47, 1435, 1393.47, 1295.46, 1253, 1023.39, 844.30, 638.37, 558.89, 424.22; ES-MS: m/z 349 (72%), 327 (100%), 203 (70%).

1,2-Bis(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl)disulfane (7)

^{1}H NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 2.174 (*s*, 3H), 2.257; (*s*, 3H), 3.672-3.628 (*t*, J= 6.6 Hz, 2H), 4.303-4.259 (*t*, J= 6.6 Hz, 2H), 5.722 (*s*, 1H); ^{13}C NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 148.20, 139.12, 105.25, 49.65, 30.21, 13.61, 11.16; IR: *v* (cm^{-1}) 2962.13, 2924.33, 2855.57, 1645.82, 1556.82, 1425.83, 1382.36, 1281.77, 970.35, 956.35, 779.98, 697.44, 664.29, 437.00, 413.46; ES-MS: *m/z* 301.2 (15%), 205.2 (100%), 175.2 (20%), 155.4 (10%), 123.5 (15%), 107.4 (10%).

1,2-Bis(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl)ditellane (8)

^{1}H NMR ($CDCl_3$/CCl_4, 400 MHz): δ ppm 2.183 (*s*, 3H), 2.246 (*s*, 3H), 2.936-2.899 (*t*, J = 7.6 Hz, 2H), 4.262-4.225 (*t*, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 147.28, 138.07, 104.89, 50.46, 13.37, 10.99, 2.08 IR: *v* (cm^{-1}) 2920.28, 2872.24, 1551.75, 1458.94, 1420.20, 1293.40, 1022.68, 747.48, 661.87, 470.46; ES-MS: *m/z* 407.2 (5%), 375 (5%), 253 (100%), 125 (5%).

1,2-Bis(2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane (9)

^{1}H NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 2.101 (*s*, 3H), 2.170 (*s*, 3H), 3.208-3.161 (*t*, J = 6.9 Hz, 2H), 4.281-4.171 (*t*, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$/CCl_4, 300 MHz): δ ppm 144.91, 135.08, 50.00, 28.20, 11.43, 9.55; ^{77}Se NMR ($CDCl_3$/CCl_4): δ ppm 295.58; IR: *v* (cm^{-1}) 2933.53, 1475.32, 1405.27, 1290.59, 1248.56, 1106.79, 1075.32, 944.64, 862.11, 790.32, 730.50, 654.96, 597.36, 528.48; ES-MS: m/z 496 (100%), 474 (70%), 237 (90%), 203 (60%).

1,2-Bis(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) disulfane (10a)

^{1}H NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 2.151 (*s*, 3H), 2.228 (*s*, 3H), 3.800-3.747 (*t*, J = 6.3 Hz, 2H), 4.216-4.162 (*t*, J = 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 145.31, 145.29, 135.74, 107.85, 50.69, 42.47, 11.36, 9.45; IR: ν (cm^{-1}) 2940.15, 1677.50, 1503.91, 1340.94, 1401.58, 1386.21, 1108.52, 978.68, 941.07, 787.86, 713.87, 652.31, 480.00; ES-MS: *m/z* 86 (100%), 207 (17%).

1,2-Bis(2-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselane (10b)

^{1}H NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 2.176 (*s*, 3H), 2.258 (*s*, 3H), 3.263-3.215 (*t*, J = 6.9 Hz, 2H), 4.299-4.252 (*t*, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 145.31, 135.74, 107.85, 50.69, 42.47, 11.36, 9.45; ^{77}Se NMR ($CDCl_3/CCl_4$): δ ppm 294.53; IR: ν (cm^{-1}) 2925.36, 1560.61, 1475.75, 1405.51, 1385.27, 1290.89, 1248.58, 1178.56, 1107.05, 1075.59, 944.74, 862.31, 790.50, 730.75, 655.17, 597.71 456.78; ES-MS: *m/z* 453.5 (5%), 281.0 (100%), 203.10 (5%).

1-(2-(2-(2-(4-Formyl-3,5-dimethyl-1H-pyrazol-1-yl)ethyl) diselanyl)ethyl)-3,5-dimethyl-1H-pyrazole-4-carbaldehyde (11)

^{1}H NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 2.399 (*s*, 3H), 2.519 (*s*, 3H), 3.314-3.247 (*t*, J = 6.9 Hz, 2H), 4.323-4.255 (*t*, J = 6.9 Hz, 2H), 9.872 (*s*, 1H) ^{13}C NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 184.29, 151.37, 48.75, 27.72, 12.53, 10.30; ^{77}Se NMR ($CDCl_3/CCl_4$): δ ppm 295.82; IR: ν (cm^{-1}) 2937.62, 1655.15, 1552.96, 1474.92, 1404.90, 1385.11, 1290.85, 1248.71, 1178.99, 1106.70, 1075.14, 944.47, 861.90, 790.12, 730.26, 654.70, 597.12, 428.34; ES-MS: *m/z*: 485.10 (100%), 231.10 (25%).

General procedure for the synthesis of symmetrical substituted 1-(2-chloroethyl)pyrazolemonoselenides

In a 50 ml, 3-necked round bottomed flask was introduced 50 mL ethanol and 1g (2.658 mmol) of selenium and stirred in an inert atmosphere. To this, solution was added 0.114 g (3.0 mmol) of sodium borohydride in portions. Formation of colorless solution after some time indicated formation of sodium hydrogen selenide. To this, solution was added 0.258 g (0.915 mmol) of 1-(2-chloroethyl)-3,5-dimethyl-1H-pyrazole/4-chloro-1-(2-chloroethyl)-3,5-dimethyl-1H-pyrazole dropwise with the help of a syringe. The reaction was then allowed to stir for another 2 hours at room temperature. After the completion of the reaction as indicated by TLC, the reaction mixture was extracted by diethyl ether and the organic layer was evaporated over a rotary evaporator after drying over anhydrous sodium sulfate. Purification by column chromatography using hexane:ethyl acetate as eluent gave the pure symmetrical substituted pyrazole selenide in a good yield.

Bis(2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyl)selane (12)

^{1}H NMR ($CDCl_3/CCl_4$, 400 MHz): δ ppm 2.099 (*s*, 3H), 2.184 (*s*, 3H), 2.769-2.722 (*t*, J = 6.9 Hz, 2H), 4.073-4.025 (*t*, J = 6.9 Hz, 2H), 5.638 (*s*, 1H); ^{13}C NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm: 147.58, 138.61, 105.07, 49.10, 23.36, 13.57, 11.19; IR: ν (cm^{-1}) 2929. 45, 1553.68, 1475.84, 1405.49, 1385.24, 1291.13, 1248.67, 1178.64, 1107.22, 1075.61, 944.69, 862.30, 790.56, 730.62, 597.90, 424.15; ES-MS: *m/z* 389.1 (10%), 327.2 (27%), 203 (100%).

Bis(2-(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)ethyl)selane (13)

^{1}H NMR ($CDCl_3/CCl_4$, 400 MHz): δ ppm 2.152 (*s*, 3H), 2.226 (*s*, 3H), 2.827-2.780 (*t*, J = 6.9 Hz, 2H), 4.131-4.083 (*t*, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3/CCl_4$, 300 MHz): δ ppm 144.90, 135.14, 50.13, 23.21, 11.48, 9.58; ^{77}Se NMR ($CDCl_3/CCl_4$): δ ppm 139.75; IR: ν (cm^{-1}) 2919.24, 1549.11, 1475.12, 1406.89, 1385.95, 1291.79, 1257.93, 1180.76, 1084.69, 872.37, 857.77, 800.97, 654.41, 601.15, 541.13, 406.86; ES-MS: *m/z* 237.0 (100%), 395.1 (15%).

CONCLUSION

A successful attempt was made to synthesize some symmetrical substituted 1-(2-chloroethyl)pyrazole di/monochalcogenides from their corresponding substituted pyrazole derivatives using sodium borohydride in ethanol. Most of the compounds are solids, obtained in good yield, and are fairly soluble in all polar organic solvents. The hitherto unknown compounds obtained during the present investigations are well characterized through various spectroscopic techniques, namely, FTIR, ^{1}H NMR, ^{13}C NMR, Mass spectroscopy, and ^{77}Se NMR and X-ray in some representative cases.

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