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Synthesis of novel N-, S-substituted-polyhalo-1, 3-butadienes and crystal structure of dibutadienyl homopiperazine

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Abstract. Polyhalogenated-2-nitro-1, 3-butadienes are important synthetic precursors for a variety of polyfunctionalized bioactive heterocycles. Herein, we report the reactions of 1, 1, 3, 4, 4-pentachloro-2-nitro-1, 3-butadiene **1** and 4-bromo-1, 1, 3, 4-tetrachloro-2-nitro-1, 3-butadiene **2** with amino and thiol containing nucleophiles to obtain highly functionalized (E)-polyhalodiene-2-nitro-1, 3-butadiene derivatives. Most of these reactions were found to be highly selective resulting in good to high yields of the products. All new compounds have been characterized by nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS) and Fourier transform infrared spectroscopy (FT-IR) spectroscopic data. Single crystal X-ray structure analysis of compound **8c** is reported.

Keywords. Piperazine; homopiperazine; thiomorpholine; 1, 3-butadiene; *E*-isomers; X-ray structure.

1. Introduction

Nitro-substituted polyhalogeno-1, 3-butadienes have proven to be valuable synthetic precursors for a variety of polyfunctionalized bioactive heterocycles due to their stepped reactivity in S_N reactions.[1] Often, the building block of choice is 2-nitroperchloro-1, 3-butadiene (**1**, **2**), which is easily accessible by the introduction of an activating and directing nitro group into 2*H*-pentachloro-1, 3-butadiene. Synthetic use of (**1**, **2**) opens access to a quite diverse chemistry, the documentation of which was started by our group recently.[1,2] The preferred primary reaction centre of (**1**, **2**) is the activated terminal carbon atom C-1 of the nitrodichlorovinyl moiety. This carbon atom allows for an attack by different nucleophiles in S_NVin processes. Under harsher conditions, the internal carbon atom, C-3, is additionally open to the attack of nucleophiles.

In literature, many studies are reported on the biodegradation of morpholine with strains of *Mycobacterium* or *Arthrobacter* and Gram negative bacteria.[3–6] Thiomorpholine analogues have found applications in medicine and agriculture.[7] *N*-arylpiperazines, *N*-arylindoles, *N*-arylpyrroles and substituted anilines are important compounds, particularly, in pharmaceutical research and also as intermediates of synthesis. The *N*-arylpiperazine subunit is embedded in several pharmacologically interesting targets such as compounds related to the serotonine ligands, calcium blockers, antipsychotic drugs, antihypertensive and acetylcholinesterase inhibitory activity.[8–12]

We have reported that some N-, S-, O-substituted polyhalo-2-nitro-1, 3-butadiene compounds were synthesized from reactions of 1, 1, 3, 4, 4-pentachloro-2-nitro-1, 3-butadiene **1** and 1, 1, 3, 4-tetrachloro-4-bromo-2-nitro-1, 3-butadiene **2** with N-, S-nucleophiles.[13–17] In this study, we present the results of various reactions of 1, 1, 3, 4, 4-pentachloro-, 1, 1, 3, 4-tetrachloro-4-bromo-, and also 1-mono(alkylthio)-polyhalo-2-nitro-1, 3-butadiene with S-, S, S-, and N, S- nucleophiles as well as some additional conversions of the resulting compounds and characterization of their structures by using micro-analysis, Fourier transform infrared spectroscopy (FT-IR), ^{1}H-nuclear magnetic resonance spectroscopy (NMR), ^{13}C-NMR and mass spectrometry (MS). In addition, single crystal structure of compound **8c**[18] was solved by using X-ray diffraction method.

2. Experimental

2.1 *General apparatus*

Melting points were measured on a Buchi B-540 melting point apparatus. Elemental analyses were

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performed on a Thermo Finnigan Flash EA 1112 Elemental analyser. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FT-IR spectrometry. ^{1}H and ^{13}C NMR spectra were recorded on Varian UNITYINOVA operating at 500 MHz. Chemical shifts δ (ppm) are reported relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ refer to the solvent signal centre at $\delta = 7.26$ ppm and $\delta = 77.0$ ppm, respectively. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer according to electron spray ionization (ESI) probe. Products were isolated by column chromatography on silica gel (Fluka Silica gel 60, particle size 63–200 μm). Analytical thin-layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254) based on Merck DC-plates (aluminum-based). Visualization of the chromatogram was performed by UV light (254 nm). All chemicals were reagent grade and used without further purification. Moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. Solvents, unless otherwise specified, were of reagent grade and distilled once prior to use.

2.2 *Crystal structure determination and refinement*

Yellow crystals of compound **8c**[18] suitable for X-ray diffraction analysis were obtained by slow evaporation of ethanol solution at room temperature. A yellow single crystal of compound **8c**, $C_{21}H_{28}Cl_6N_4O_4S_2$, having approximate dimensions of 0.60 × 0.10 × 0.10 mm was mounted on a glass fibre. All measurements were made on a Rigaku R-Axis Rapid-S imaging plate area detector with graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). The data were collected at room temperature to a maximum 2θ value of 50.2°. Experimental conditions are summarized in table 1. The structure was solved by SIR 92[19] and refined with CRYSTALS.[20] The non-hydrogen atoms were refined anisotropically. H atoms were located in geometrically idealized positions C–H = 0.95(6) Å and treated as riding and $U_{iso}(H) = 1.2U_{eq}(C)$. The selected bond distances, bond and torsion angles for compound **8c** are listed in tables 2 and 3, respectively. Drawings were performed with the program ORTEP-III[21] with 50% probability displacement ellipsoide for compound **8c** in figure 1. Crystallographic data (excluding structure factors) for the structure reported in this study have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-907293 for **8c**.[22]

Table 1. Crystal data and refinement parameters for compound **8c**.

CCDC deposit number	CCDC 907293
Empirical formula	$C_{21}H_{28}Cl_6N_4O_4S_2$
Crystal colour, habit	Yellow, chunk
Formula weight	677.31
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/*n*
Cell dimensions	$a = 7.9290(6)$ Å, $b = 12.4335(8)$ Å $c = 31.167(2)$ Å $\beta = 95.504(4)°$
Volume	3058.5(4) Å^3
Z	4
Density (calculated)	1.471 mg/m^3
Absorption coefficient	0.731 mm^{-1}
F_{000}	1392.00
Index ranges	$-9 \le h \le 8$ $-14 \le k \le 14$ $-37 \le l \le 36$
Reflections collected	24008
Independent reflections	5444 [$R_{int} = 0.083$]
Data/restraints/parameters	4570/0/334
Goodness of fit indicator	1.266
Final R indices [$I > 2\sigma(I)$]	$R = 0.088$, $wR = 0.045$
Largest difference peak and hole	0.54 and −0.47 e.Å^{-3}

Table 2. Selected bond distances (Å) for compound **8c**.

Atom	Distance (Å)	Atom	Distance (Å)
C1–C2	1.29(1)	N2–C13	1.47(1)
C2–C3	1.44(1)	C12–C13	1.51(1)
C3–C4	1.43(2)	N3–C12	1.49(1)
N2–C9	1.47(1)	C14–C15	1.43(2)
C9–C10	1.52(1)	C15–C16	1.42(2)
C10–C11	1.51(1)	C16–C17	1.30(2)

2.3 *Synthesis of S-, S, S-, S, S, S- and N, S-substitute nitrodienes*

Method 1: Equimolar amounts of polyhalo-2-nitrodiene (**1** and **2**) and thiols were mixed directly or in dichloromethane and stirred between 12–48 h at room temperature. The yields of reaction were extracted with chloroform (20 mL) and water (20 mL) and dried with sodium sulphate (Na_2SO_4). The residues were purified by column chromatography on silica gel.

Method 2: Polyhalo-2-nitrodiene (**1** and **2**) and three molar equivalent thiols were dissolved in ethanol (25 mL) and added to the solution of sodium hydroxide in ethanol and stirred between 12 and 48 h at room

Table 3. Selected bond and torsion angles (°) for compound **8c**.

Atom	Bond angle (°)	Atom	Torsion angle (°)
C1–C2–C3	125.0(9)	C1–C2–C3–C4	−56.0(1)
C2–C3–C4	122.3(9)	C14–C15–C16–C17	64.0(1)
C14–C15–C16	122.0(1)	C1–C2–C3–N1	127.0(1)
C15–C16–C17	123.0(1)	C17–C16–C15–N4	−114.0(1)
C9–N2–C13	113.7(8)	N2–C9–C10–C11	91.0(1)
C11–N3–C12	115.2(8)	N2–C13–C12–N3	−68.0(1)
C9–C10–C11	113.6(8)	C5–C6–C7–C8	174.0(1)
O1–N1–O2	122.9(9)	C18–C19–C20–C21	−168.0(2)

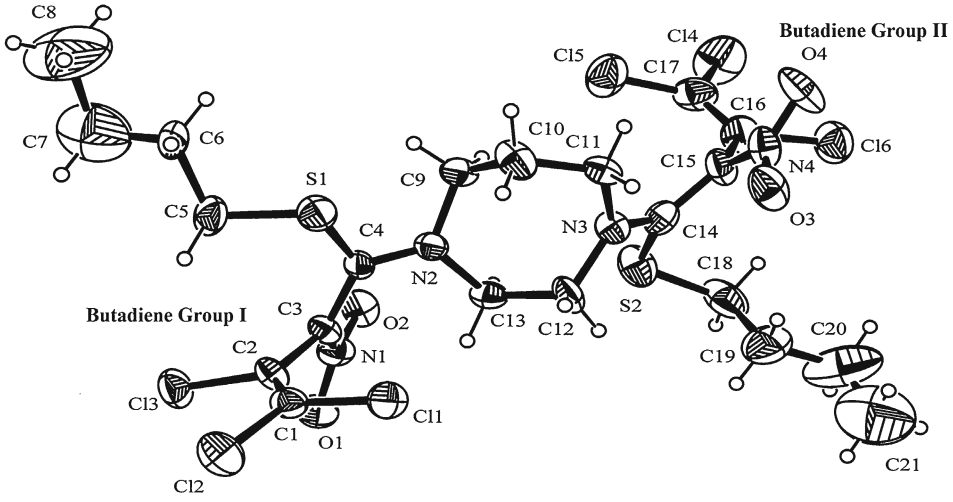


Figure 1. Molecular structure of the compound **8c**. Displacement ellipsoids are drawn at 50% probability level.

temperature. The yields of reaction were extracted with chloroform (20 mL) and water (20 mL) and dried with sodium sulphate (Na_2SO_4). After the solvent was evaporated, the residue was purified by column chromatography on silica gel.

Method 3: S-monothiosubstituted-2-nitro-1, 3-butadiene and thiomorpholine and some piperazine derivatives were dissolved in dichloromethane (25 mL) and stirred between 12 and 48 h at room temperature. The yields of reaction were extracted with chloroform (20 mL) and water (20 mL) and dried with sodium sulphate (Na_2SO_4). The residues were purified by column chromatography on silica gel.

2.3a *1, 3, 4, 4-Tetrachloro-2-nitro-(1E)-(pentylsulphanyl)-1, 3-butadiene (**4d**)*: Compound **4d** was synthesized from reaction of **1** (2 g, 7.37 mmol) with pentanethiol **3d** (0.76 g, 7.37 mmol) according to method 1. Yield: 1.88 g (75%); Yellow oil. R_f (CCl_4): 0.41; IR(KBr, cm^{-1}): ν = 2874, 2935, 2965 (C–H), 1462, 1605 (C=C), 1292, 1535 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.8 (t, J = 6.83 Hz, 3H, CH_3), 1.0–1.5 (m, 4H, $2CH_2$), 1.7 (m, 2H, S–CH_2–CH_2), 3.1 ppm (t, J = 7.32 Hz, 2H, S–CH_2). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 14.08 (CH_3), 22.39, 28.32 (CH_2), 29.93 (S–CH_2–CH_2), 31.08 (S–CH_2), 121.86, 128.80, 138.77, 158.37 ppm (C_{butad}). Anal. $C_9H_{11}N_1O_2S_1Cl_4$ (M = 339.07 g/mol). Micro analysis: Calcd. C, 31.88; H, 3.27; N, 4.13; S, 9.45. Found C, 31.89; H, 3.25; N, 4.14; S, 9.48%.

2.3b *1, 3, 4, 4-Tetrachloro-2-nitro-(1E)-(2-ethyl-hexyl-sulphanyl)-1, 3-butadiene (**4h**)*: Compound **4h** was synthesized from reaction of **1** (2 g, 7.37 mmol) with 2-ethyl-hexanethiol **3h** (1.07 g, 7.37 mmol) according to method 1. Yield: 1.85 g (66%); Yellow oil. R_f (CCl_4): 0.41; IR(KBr, cm^{-1}): ν = 2960, 2929, 2872, 2859 (C–H), 1460, 1603 (C=C), 1292, 1537 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.8–0.9 (t, J = 6.83 Hz, 6H, $2CH_3$), 1.2–1.4 (m, 8H, $4CH_2$), 1.7 (m, 1H, S–CH_2–CH), 3.0 ppm (d, 2H, S–CH_2). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 13.00, 13.02 (CH_3), 21.82, 24.65, 27.66, 27.75 (CH_2), 31.24 (S–CH_2–CH), 37.66 (S–CH_2), 120.65, 127.55, 137.72, 157.22 ppm (C_{butad}). Micro analysis: $C_{12}H_{17}N_1O_2S_1Cl_4$

(M = 381.151 g/mol). Calcd. C, 37.80; H, 4.49; N, 3.67; S, 8.41. Found C, 37.89; H, 4.45; N, 3.64; S, 8.48%.

2.3c *3, 4, 4-Trichloro-2-nitro-(1E)-[pentylsulphanyl-4-(thiomorpholin-1-yl)]-1, 3-butadiene (**5d**)*: Compound **5d** was synthesized from reaction of **4d** (0.5 g, 1.47 mmol) with thiomorpholine (0.15 g, 1.47 mmol) according to method 3. Yield: 0.48 g (81%); Yellow oil. R_f (CCl_4): 0.48; IR (KBr, cm^{-1}): ν = 2857, 2928, 2858 (C–H), 1522, 1652 (C=C), 1270, 1522 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ 0.85 (t, J = 7.32 Hz, 3H, CH_3), 1.2–1.4 (m, 4H, CH_2), 1.6 (m, 2H, S–CH_2–CH_2), 2.90 (t, J = 5.37 Hz, 2H, S–CH_2), 2.65 (t, J = 4.88 Hz, 4H, $H_{thiomorp}$), 3.40 ppm (s, br, 4H, $H_{thiomorp}$); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ 12.80 (CH_3), 21.11, 26.87 (CH_2), 29.82 (S–CH_2–CH_2), 34.42 (S–CH_2), 43.46, 54.98 ($C_{thiomorp}$), 118.17, 123.81, 132.87, 169.60 ppm (C_{butad}); Micro analysis: $C_{13}H_{19}N_2O_2S_2Cl_3$ (M, 405.79). Calcd. C, 38.47; H, 4.71; N, 6.90; S, 15.80 Found C, 38.24; H, 4.64; N, 6.80; S, 15.85%.

2.3d *3, 4, 4-Trichloro-2-nitro-(1E)-[ethylsulphanyl-1-(1-piperonylpiperazin-1-yl)]-1, 3-butadiene (**7a**)*: Compound **7a** was synthesized from reaction of **4a** (0.5 g, 1.68 mmol) with 1-(piperonyl)piperazine **6a** (0.37 g, 1.68 mmol) according to method 3. Yield: 0.52 g (64%); m.p.: 228–229°C. R_f: 0.65 (CH_2Cl_2). IR (KBr, cm^{-1}): ν = 3053 (Ar–H), 2925, 2852, 2809, 2771 (C–H), 1523, 1596 (C=C), 1289, 1450 (C–NO_2). ^{1}H-NMR (499.74 MHz, $CDCl_3$): δ = 1.18 (t, J = 7.81 Hz, 3H, CH_3), 2.5 (sbr, 4H, H_{piper}), 2.9 (t, J = 7.32 Hz, 2H, S–CH_2), 3.4 (s, 2H, N–CH_2), 3.6 (sbr, 4H, H_{piper}), 5.88 (s, 2H, O–CH_2–O), 6.6–6.9 ppm (m, 3H, H_{arom}). ^{13}C-NMR (125.66 MHz, $CDCl_3$): δ = 13.90 (CH_3), 28.74 (S–CH_2), 51.33, 61.05 (N–CH_2), 100.06 (N–CH_2), 107.06 (O–CH_2–O), 108.34, 117.20, 121.33, 123.54, 125.85, 146.15, 146.94, 167.64 ppm ($CH_{arom,}$ $C_{arom,}$ C_{butad}). MS [+ESI]: m/z 504 $[M+Na]^+$, 482 $[M]^+$, MS/MS[+ESI]: m/z 446 $[M–Cl]^+$, 400 $[M–(Cl+NO_2)]^+$, 365 $[M–(2Cl+NO_2)]^+$, 332 $[M–(3Cl+NO_2)]^+$, 309 $[M–(3Cl+NO_2+Na+H)]^+$. Micro analysis: $C_{18}H_{20}N_3O_4S_1Cl_3$ (M, 480.801). Calcd. C, 44.96; H, 4.19; N, 8.73; S, 6.66. Found C, 44.92; H, 4.14; N, 8.74; S, 6.61%.

2.3e *3, 4, 4-Trichloro-2-nitro-(1E)-[propylsulphanyl-1-(1-piperonylpiperazin-1-yl)]-1, 3-butadiene (**7b**)*: Compound **7b** was synthesized from reaction of **4b** (1.0 g, 3.21 mmol) with 1-(piperonyl)piperazine **6a** (0.70 g, 3.21 mmol) according to method 3. Yield: 0.82 g (52%); Yellow oil. R_f: 0.60 (CH_2Cl_2). IR (KBr, cm^{-1}): ν = 3051 (Ar–H), 2963, 2831, 2814, 2776 (C–H), 1528, 1656 (C=C), 1274, 1442 (C–NO_2). ^{1}H-NMR (499.74 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.32 Hz, 3H, CH_3), 1.5–1.7 (m, 2H, S–CH_2–CH_2), 2.6 (sbr, 4H, H_{piper}), 2.9 (t, J = 6.83 Hz, 2H, S–CH_2), 3.4 (s, 2H, N–CH_2), 3.6 (sbr, 4H, H_{piper}), 5.87(s, 2H, O–CH_2–O), 6.6–6.9 ppm (m, 3H, H_{arom}). ^{13}C-NMR (125.66 MHz, $CDCl_3$): δ = 12.25 (CH_3), 22.22 (S–CH_2–CH_2, 36.32 (S–CH_2), 51.18, 60.92 (N–CH_2), 100.09 (N–CH_2), 107.09 (O–CH_2–O), 108.47, 116.98, 121.55, 123.55, 125.89, 146.26, 146.94, 168.10 ppm (CH_{arom}, C_{arom}, C_{butad}). MS [+ESI]: m/z 557 $[M+Na+K]^+$, MS/MS[+ESI]: m/z 496 $[M+H]^+$, 459 $[M–Cl]^+$, 413 $[M–(Cl+NO_2)]^+$, 346 $[M–(3Cl+NO_2)]^+$, 323 $[M–(3Cl+NO_2+Na+H)]^+$. Micro analysis: $C_{19}H_{22}N_3O_4S_1Cl_3$ (M, 494.832). Calcd. C, 46.11; H, 4.48; N, 8.49; S, 6.47. Found C, 46.22; H, 4.44; N, 8.54; S, 6.51%.

2.3f *3, 4, 4-Trichloro-2-nitro-(1E)-[pentylsulphanyl-4-(2-fluorophenylpiperazin-1-yl)]-1, 3-butadiene (**7c**)*: Compound **7c** was synthesized from reaction of **4d** (0.5 g, 1.47 mmol) with 2-fluorophenylpiperazine **6b** (0.26 g, 1.47 mmol) according to method 3. Yield: 0.5 g (71%); Yellow oil. R_f: 0.50 ($CHCl_3$). IR (KBr pellet, cm^{-1}): ν = 3045, 3020 (Ar–H), 2957, 2928, 2856 (C–H), 1529, 1655 (C=C), 1275, 1501 (C–NO_2). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.8 (t, J = 6.83 Hz, 3H, CH_3), 1.1–1.4 (m, 4H, CH_2), 1.6 (m, 2H, S–CH_2–CH_2), 3.0 (t, J = 7.32 Hz, 2H, S–CH_2), 3.2 (s, br, 4H, H_{piper}), 3.8 (s, br, 4H, H_{piper}), 6.8–7.1 ppm (m, 4H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.81 (CH_3), 21.11, 28.47 (CH_2), 29.81 (S–CH_2−CH_2), 34.55 (S–CH_2), 49.40, 52.34 (N–CH_2), 115.44, 122.92, 122.98, 123.68, 123.70, 125.84, 137.37, 153.81, 155.78, 168.39 ppm ($CH_{arom,}$ $C_{arom,}$ C_{butad}). Micro analysis: $C_{19}H_{23}O_2S_1N_3Cl_3F$ (M, 482.83). Calcd. C, 47.26; H, 4.80; N, 8.70; S, 6.64. Found: C, 47.89; N, 8.75; H, 4.67; S, 6.02%.

2.3g *3, 4, 4-Trichloro-2-nitro-(1E)-[pentylsulphanyl-4-4-fluorophenylpiperazin-1-yl)]-1, 3-butadiene (**7d**)*: Compound **7d** was synthesized from reaction of **4d** (0.5 g, 1.47 mmol) with 4-fluorophenylpiperazine **6c** (0.26 g, 1.47 mmol) according to method 3. Yield: 0.45 g (63%); Yellow oil. R_f: 0.50 ($CHCl_3$). IR (KBr, pellet, cm^{-1}): ν = 3055, 3019 (Ar–H), 2955, 2932, 2870 (C–H), 1540, 1654 (C=C), 1271, 1509 (C–NO_2). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.83 Hz, 3H, CH_3), 1.1–1.4 (m, 4H, CH_2), 1.6 (m, 2H, S–CH_2–CH_2), 2.9 (t, J = 7.32 Hz, 2H, S–CH_2), 3.2 (s, br, 4H, H_{piper}), 3.8 (s, br, 4H, H_{piper}), 6.8–7.1 ppm

(m, 4H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.81 (CH_3), 21.11, 28.45 (CH_2), 29.79 (S–CH_2–CH_2), 34.58 (S–CH_2), 49.78, 51.81 (N–CH_2), 115.19, 120.78, 121.60, 123.89, 125.71, 144.62, 158.48, 159.67, 168.34 ppm ($CH_{arom,}$ $C_{arom,}$ C_{butad}). Micro analysis: $C_{19}H_{23}O_2S_1N_3Cl_3F$ (M, 482.83). Calcd. C, 47.26; H, 4.80; N, 8.70; S, 6.64. Found: C, 47.38; H, 4.84; N, 8.90; S, 6.62%.

2.3h *3, 4, 4-Trichloro-2-nitro-(1E)-[pentylsulphanyl-1-(4-diphenylmethyl)piperazin-1-yl)]-1, 3-butadiene (**7e**)*: Compound **7e** was synthesized from reaction of **4d** (0.5 g, 1.47 mmol) with *N*-(diphenylmethyl)-piperazine **6d** (0.37 g, 1.47 mmol) according to method 3. Yield 0.56 g (69%); Yellow oil. R_f ($CHCl_3$): 0.38; IR (KBr pellet, cm^{-1}): ν = 3060, 3027 (Ar–H), 2858, 2928 (C–H), 1597, 1660 (C=C), 1286, 1530 (C–NO_2); ^1H NMR (499.74 MHz, $CDCl_3$): δ 0.82 (t, J = 6.83 Hz, 3H, CH_3), 1.1–1.4 (m, 4H, CH_2), 1.5–1.6 (m, 2H, S–CH_2–CH_2), 2.85 (t, j = 7.32 Hz, 2H, S–CH_2), 2.5 (s, br, 4H, H_{piper}), 3.55 (s, br, 4H, H_{piper}), 4.4 (s, 1H, –CH<), 7.1–7.5 ppm (m, 10H, $H_{arom.}$); ^{13}C NMR (125.66 MHz, $CDCl_3$): δ 12.80 (CH_3), 21.08, 28.44 (CH_2), 29.73 (S–CH_2–CH_2), 34.44 (S–CH_2), 35.85, 50.54 (N–CH_2), 75.79 (–CH<), 123.55, 125.56, 125.90, 126.50, 127.88, 129.01, 140.48, 167.80 ppm ($CH_{arom,}$ $C_{arom,}$ C_{butad}). Micro analysis: $C_{26}H_{30}N_3O_2S_1Cl_3$ (M, 554.971). Calcd. C, 56.27; H, 5.44; N, 7.57; S, 5.77. Found C, 56.47; H, 5.14; N, 7.59; S, 5.70%.

2.3i *3, 4, 4-Trichloro-2-nitro-(1E)-[hexadecylsulphanyl-1-(1-piperonylpiperazin-1-yl)]-1, 3-butadiene (**7f**)*: Compound **7f** was synthesized from reaction of **4f** (0.5 g, 1.01 mmol) with 1-(piperonyl) piperazine **6a** (0.22 g, 1.01 mmol) according to method 3. Yield: 0.45 g (66%); m.p.: 188–189°C. R_f: 0.55 (CH_2Cl_2). IR (KBr, cm^{-1}): ν = 3055 (Ar–H), 2924, 2853, 2775 (C–H), 1530, 1607 (C=C), 1275, 1490 (C–NO_2). ^1H-NMR (499.74 MHz, $CDCl_3$): δ = 0.79 (t, J = 6.35 Hz, 3H, CH_3), 1.0–1.4 (m, 26H, CH_2), 1.6 (m, 2H, S–CH_2–CH_2), 2.6 (sbr, 4H, H_{piper}), 2.9 (t, J = 6.35 Hz, 2H, S–CH_2), 3.5 (s, 2H, N–CH_2), 3.6 (sbr, 4H, H_{piper}), 5.9 (s, 2H, O–CH_2–O), 6.6–6.9 ppm (m, 3H, H_{arom}). ^{13}C-NMR (125.66 MHz, $CDCl_3$): δ = 13.10 (CH_3), 21.67, 27.52, 27.66, 28.02, 28.22, 28.33, 28.36, 28.50, 28.59, 28.63, 28.67, 28.68, 28.72, 30.90 (CH_2), 34.50 (S–CH_2–CH_2), 38.25 (S–CH_2), 51.12, 60.91 (N–CH_2), 100.11 (N–CH_2), 107.12 (O–CH_2–O), 108.52, 117.02, 121.63, 123.58, 125.87, 146.34, 146.97, 168.13 ppm ($CH_{arom,}$ $C_{arom,}$ C_{butad}). MS [+ESI]: m/z 739 $[M+Na+K]^+$, 701 $[M+Na]^+$, 678 $[M]^+$, MS/MS[+ESI]: m/z 642 $[M–Cl]^+$, 596 $[M–(Cl+NO_2)]^+$, 528 $[M–(3Cl+NO_2)]^+$, 505 $[M–(3Cl+NO_2+Na)]^+$. Micro analysis: $C_{32}H_{48}N_3O_4S_1Cl_3$ (M, 677.181). Calcd. C, 56.75; H, 7.14; N, 6.20; S, 4.73. Found C, 56.78; H, 7.24; N, 6.24; S, 4.75%.

2.3j *1, 1′-Bis[3, 4, 4-trichloro-(1E)-(2-ethyl-hexyl-sulphanyl)-2-nitro-1, 3-butadienyl]-homopiperazine (**8h**)*: Compound **8h** was synthesized from reaction of **4h** (0.5 g, 1.31 mmol) with homopiperazine (0.13 g, 1.31 mmol) according to method 2. Yield: 0.65 g (63%); Yellow oil. R_f (CH_2Cl_2): 0.48; IR(KBr, cm^{-1}): ν = 2960, 2929, 2869, 2859 (C–H), 1455, 1672 (C=C), 1277, 1568 (C–NO_2); ^1H NMR (499.74 MHz, $CDCl_3$): δ = 0.8–0.9 (t, J = 6.83 Hz, 6H, $2CH_3$), 1.1–1.4 (m, 8H, $4CH_2$), 1.55 (m, 1H, S–CH_2–CH), 3.0 (d, 2H, S–CH_2), 2.2 (s, br, $H_{homopiper}$), 3.8 ppm (s, br, $H_{homopiper}$). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.68, 12.99, 13.10, 13.18 (CH_3), 21.67, 21.79, 24.47, 27.57, 27.77, 28.17, 28.63, 28.68 (CH_2), 30.90, 31.16 (S–CH_2–CH), 38.52, 39.40 (S–CH_2), 117.77, 124.11, 125.46, 171.69 ppm (C_{butad}). MS [+ESI]: m/z 790 $[M]^+$, 743 $[M–NO_2]^+$. Micro analysis: $C_{29}H_{44}N_4O_4S_2Cl_6$ (M = 789.545 g/mol). Calcd. C, 44.11; H, 5.61; N, 7.09; S, 8.12. Found C, 44.18; H, 5.65; N, 7.09; S, 8.16%.

2.3k *3, 4, 4-Trichloro-2-nitro-(1E)-[(2-ethyl-hexyl-sulphanyl)-1-homopiperazinyl]-1, 3-butadiene (**9h**)*: Compound **9h** was synthesized from reaction of **4h** (0.5 g, 1.31 mmol) with homopiperazine (0.13 g, 1.31 mmol) according to method 3. Yield: 0.12 g (12%); Yellow oil. R_f (CH_2Cl_2): 0.45; IR(in $CHCl_3$, cm^{-1}): ν = 3849 (N–H), 2958, 2919, 2850 (C–H), 1486, 1696 (C=C), 1278, 1506 (C–NO_2); ^1H NMR (499.74 MHz, $CDCl_3$): δ = 0.8 (t, J = 7.32 Hz, 6H, $2CH_3$), 1.0–1.4 (m, 8H, $4CH_2$), 1.5 (m, 1H, S–CH_2–CH), 3.0 (d, 2H, S–CH_2), 2.0 (s, br, $H_{homopiper}$), 3.6 (s, br, $H_{homopiper}$), 5.3 ppm (s, 1H, NH). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.97, 13.63 (CH_3), 21.80, 24.46, 27.55, 28.68 (CH_2), 31.15 (S–CH_2–CH), 38.59 (S–CH_2), 108.74, 131.55, 154.84, 178.34 ppm (C_{butad}). MS [+ESI]: m/z 540 $[M+4Na+3H]^+$. Micro analysis: $C_{17}H_{28}N_3O_2S_1Cl_3$ (M = 444.855 g/mol). Calcd. C, 45.90; H, 6.34; N, 9.44; S, 7.20. Found C, 45.92; H, 6.38; N, 9.49; S, 7.26%.

2.3l *3, 4, 4-Trichloro-2-nitro-1-bis(11-sulphanyl-1-undecanol)-1, 3-butadiene (**10e**)*: Compound **10e** was synthesized from reaction of **1** (2 g, 7.37 mmol) with 11-mercapto-1-undecanol **3e** (4.51 g, 22.06 mmol) according to method 2. Yield: 1.3 g (50%); Yellow oil. R_f: 0.50 ($CHCl_3$). IR (KBr pellet, cm^{-1}):

ν = 3338 (OH), 2926, 2853 (C–H), 1535, 1574 (C=C), 1292, 1464 (C–NO_2). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.1–1.4 (m, 28H, CH_2), 1.45–1.5 (m, 4H, S–CH_2–CH_2), 1.55–1.7 (m, 4H, HO–CH_2–CH_2), 3.0 (s, 2H, OH), 3.6 (t, J = 6.84 Hz, 4H, S–CH_2), 4.2 ppm (m, 4H, HO–CH_2).^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 23.62, 24.72, 25.85, 27.35, 27.50, 27.64, 27.67 (CH_2), 28.02, 28.04 (S–CH_2–CH_2), 28.35, 28.38 (HO–CH_2–CH_2), 28.43, 28.45 (S–CH_2), 62.11, 62.14 (HO–CH_2), 119.28, 122.13, 126.64, 161.99 ppm (C_{butad}). MS [+ESI]: m/z 608 $[M]^+$, 562 $[M–NO_2]^+$; Micro analysis: $C_{26}H_{46}O_4S_2N_1Cl_3$ (M, 607.149). Calcd. C, 51.43; H, 7.63; N, 2.30; S, 10.56. Found C, 51.42; H, 7.67; N, 2.32; S, 10.59%.

2.3m *3, 4-Dichloro-2-nitro-1, 1, 4-tris(propylsulphanyl)-1, 3-butadiene (**11b**)*: Compound **11b** was synthesized from reaction of **1** (2 g, 7.37 mmol) with propanethiol **3b** (1.68 g, 22.11 mmol) according to method 2. Yield 1.9 g (66%); Yellow oil. R_f: (petroleum ether-CCl_4(1:1)]: 0.32; IR(KBr, cm^{-1}): ν = 2990(C–H), 1560, 1630 (C=C), 1280, 1530 (C–NO_2); ^{1}H-NMR (499.74 MHz, $CDCl_3$): δ 0.95 (t, J = 7.32 Hz, 3H, CH_3), 1.60 (m, 2H, S–CH_2–CH_2), 2.95 ppm (t, J = 7.32 Hz, 2H, S–CH_2); ^{13}C-NMR (125.66 MHz, $CDCl_3$): δ 12.38 (CH_3), 22.44 (S–CH_2–CH_2), 37.41 (S–CH_2), 123.64, 127.99, 142.78, 152.55 ppm (C_{butad}); MS[+ESI]: m/z 390.24 $[M]^+$; Micro analysis: $C_{13}H_{21}N_1O_2S_3Cl_2$ (M, 390.41 g/mol). Calcd. C, 39.99; H, 5.42; N, 3.58; S, 24.63. Found C, 40.25; H, 5.75; N, 4.00; S, 23.98%.

2.3n *4, 4-Trichloro-2-nitro-1-tris(11-sulphanyl-1-undecanol)-1, 3-butadiene (**11e**)*: Compound **11e** was synthesized from reaction of **1** (2 g, 7.37 mmol) with 11-mercapto-1-undecanol **3e** (4.51 g, 22.06 mmol) according to method 2. Yield: 0.5 g (35%); Yellow oil. R_f: 0.40 ($CHCl_3$). IR (KBr pellet, cm^{-1}): ν = 3362(OH), 2924, 2851 (C–H), 1527, 1550 (C=C), 1287, 1469 (C–NO_2). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.1–1.4 (m, 35H, CH_2), 1.43–1.5 (m, 6H, S–CH_2–CH_2), 1.6–1.7 (m, 6H, HO–CH_2–CH_2), 3.1 (s, 3H, OH), 3.6 (t, J = 6.84 Hz, 6H, S–CH_2), 4.3 ppm (m, 6H, HO–CH_2). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 23.11, 23.15, 23.24, 23.62, 23.65, 24.72, 25.85, 27.35, 27.50, 27.64, 27.67 (CH_2), 28.12, 28.14 (S–CH_2–CH_2), 28.45, 28.48 (HO–CH_2–CH_2), 28.43, 28.45, 28.46 (S–CH_2), 62.11, 62.15, 62.20 (HO–CH_2), 117.28 123.13, 155.64, 162.99 ppm (C_{butad}). MS [–ESI]: m/z 758 $[M–OH]^-$; Micro analysis: $C_{37}H_{69}O_5S_3N_1Cl_2$ (M, 775.064). Calcd. C, 57.33; H, 8.97; N, 1.80; S, 12.41. Found C, 57.32; H, 8.99; N, 1.82; S, 12.38%.

2.3o *3, 4-Dichloro-2-nitro-1, 1, 3-tris(octadecylsulphanyl)-1,3-butadiene (**11g**)*: Compound **11g** was synthesized from reaction of **1** (2 g, 7.37 mmol) with octadecanethiol **3g** (6.33 g, 22.11 mmol) according to method 2. Yield: 3.2 g (43%). m.p.: 41–42°C, R_f (CCl_4): 0.54; IR (KBr, cm^{-1}): ν = 2980, 2895, 2820 (C–H), 1580, 1630 (C=C), 1280, 1530 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ 0.88 (t, J = 7.32 Hz, 3H, CH_3), 1.2–1.5 (m, 30H, CH_2), 1.60 (m, 2H, S–CH_2–CH_2), 2.95 ppm (t, J = 7.32 Hz, 2H, S–CH_2): ^{13}C NMR (125.66 MHz, $CDCl_3$): δ 13.08 (CH_3), 21.67, 27.67, 27.81, 27.83, 28.10, 28.13, 28.15, 28.26, 28.35, 28.43, 28.46, 28.57, 28.64, 28.65, 28.74 (CH_2), 30.92 (S–CH_2–CH_2), 35.57 (S–CH_2), 123.26, 128.14, 142.53, 152.84 ppm (C_{butad}); MS (+ESI): m/z 1021.81 $[M]^+$; 975.84 $[M–46]^+$; Micro analysis: $C_{58}H_{111}N_1O_2S_3Cl_2$ (M, 1021.63). Calcd. C, 68.18; H, 10.95; N, 1.37; S, 9.41. Found C, 68.25; H, 11.22; N, 1.29; S, 9.28%.

2.3p *1, 3, 4-Trichloro-4-bromo-2-nitro-(1E)-(2-ethyl-hexyl-sulphanyl)-1, 3-butadiene (**12h**)*: Compound **12h** was synthesized from reaction of **2** (2 g, 6.33 mmol) with 2-ethyl-hexanethiol **3h** (0.92 g, 6.33 mmol) according to method 1. Yield: 1.75 g (65%); Yellow oil. R_f (CCl_4): 0.38; IR(KBr, cm^{-1}): ν = 2960, 2929, 2872, 2859 (C–H), 1459, 1605 (C=C), 1312, 1533 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.8–0.9 (t, J = 6.83 Hz, 6H, $2CH_3$), 1.1–1.4 (m, 8H, $4CH_2$), 1.6 (m, 1H, S–CH_2–CH), 3.1 ppm (d, 2H, S–CH_2). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.99, 13.01 (CH_3), 21.82, 24.61, 24.65, 27.25 (CH_2), 31.21 (S–CH_2–CH), 38.52 (S–CH_2), 122.11, 124.09, 157.10, 187.81 ppm (C_{butad}). Micro analysis: $C_{12}H_{17}N_1O_2S_1Cl_3Br_1$ (M = 425.602 g/mol). Calcd. C, 33.86; H, 4.02; N, 3.29; S, 7.53. Found C, 33.89; H, 3.05; N, 3.24; S, 7.55%.

2.3q *3, 4-Dichloro-4-bromo-2-nitro-1-(E)-(2-ethlyhexyl-sulphanyl)-1-homopiperazinyl-1, 3-butadiene (**13h**)*: Compound **13h** was synthesized from reaction of **12h** (0.5 g, 1.17 mmol) with homopiperazine (0.11 g, 1.17 mmol) according to method 1. Yield: 0.18 g (17%); Yellow oil. R_f ($CHCl_3$): 0.38; IR(in $CHCl_3$, cm^{-1}): ν = 3784 (N–H), 2957, 2922, 2851 (C–H), 1429, 1667 (C=C), 1276, 1509 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.8 (t, J = 7.32 Hz, 6H, $2CH_3$), 1.0–1.4 (m, 8H, $4CH_2$), 1.6 (m, 1H, S–CH_2–CH), 3.1 (d, 2H, S–CH_2), 2.0 (s, br, $H_{homopiper}$), 3.6 (t, J = 7.32, $H_{homopiper}$), 5.2 ppm (s, 1H, NH). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.98, 13.09 (CH_3), 21.67, 21.80, 27.57, 28.34 (CH_2), 31.20 (S–CH_2–CH), 38.07 (S–CH_2), 126.40, 134.55, 155.74, 179.03 ppm (C_{butad}). MS [+ESI]: m/z 537 $[M+Na+2H]^+$. Micro analysis:

$C_{17}H_{28}N_3O_2S_1Cl_2Br_1$ (M = 489.306 g/mol). Calcd. C, 41.73; H, 5.76; N, 8.58; S, 6.55. Found C, 41.72; H, 5.75; N, 8.54; S, 6.56%.

2.3r *1, 1′-Bis[3, 4-dichloro-4-bromo-1(E)-(2-ethyl-hexyl-sulphanyl)-2-nitro-1, 3-butadienyl]homopiperazine (**14h**)*: Compound **14h** was synthesized from reaction of **12h** (0.5 g, 1.17 mmol) with homopiperazine (0.11 g, 1.17 mmol) according to method 1. Yield: 0.65 g (63%), Yellow oil. R_f ($CHCl_3$): 0.48; IR(KBr, cm^{-1}): ν = 2957, 2922, 2850 (C–H), 1463, 1647 (C=C), 1270, 1510 (C–NO_2); ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.7–0.9 (t, J = 6.83 Hz, 12H, 4CH_3), 1.1–1.4 (m, 16H, 8CH_2), 1.6 (m, 2H, S–CH_2–CH), 3.0 (d, 4H, S–CH_2), 2.2 (s, br, $H_{homopiper}$), 3.8 ppm (m, $H_{homopiper}$). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.99, 13.01, 13.10, 13.39 (CH_3), 21.67, 21.79, 24.49, 26.07, 27.58, 28.34, 28.64, 28.68 (CH_2), 30.91, 31.18 (S–CH_2–CH), 38.52, 39.34 (S–CH_2), 113.04, 126.93, 128.83, 168.27 ppm (C_{butad}). MS [+ESI]: m/z 900 $[M+Na]^+$, Micro analysis: $C_{29}H_{44}N_4O_4S_2Cl_4Br_2$ (M = 878.44 g/mol). Calcd. C, 39.65; H, 5.04; N, 6.37; S, 7.30. Found C, 39.68; H, 5.05; N, 6.39; S, 7.36%.

2.3s *3, 4-Dichloro-4-bromo-2-nitro-(1E)-[cyclo-(2-butylaminoethylsulphanyl)]-1, 3-butadiene (**15**)*: Compound **15** was synthesized from reaction of **2** (1 g, 3.16 mmol) with 2-(butylamino)ethanethiol **3i** (0.42 g, 3.16 mmol) according to method 1. Yield: 0.9 g (76%). Yellow solid. m.p.: 145–146°C. R_f: 0.50 ($CHCl_3$). IR (KBr, cm^{-1}): ν = 2951, 2932, 2869 (C–H), 1530, 1581 (C=C), 1255, 1456 (C–NO_2). ^{1}H-NMR (499.74 MHz, $CDCl_3$): δ = 0.9 (t, J = 7.32 Hz, 3H, CH_3), 1.5 (m, 4H, CH_2), 3.5 (t, J = 6.84 Hz, S–CH_2), 3.8–4.1 ppm (m, 4H, N–CH_2). ^{13}C-NMR (125.66 MHz, $CDCl_3$): δ = 12.68 (CH_3), 19.10 (CH_2), 26.22 (N–CH_2–CH_2), 28.87 (S–CH_2), 50.85, 56.36 (N–CH_2), 112.54, 124.47, 126.38, 167.03 ppm (C_{butad}). MS [+ESI]: m/z 377 $[M]^+$, 399 $[M+Na]^+$. Micro analysis: $C_{10}H_{13}O_2S_1N_2Cl_2Br_1$ (M, 376.102). Calcd. C, 31.93; H, 3.48; N, 7.44; S, 8.52. Found C, 31.92; H, 3.47; N, 7.42; S, 8.58%.

3. Results and discussion

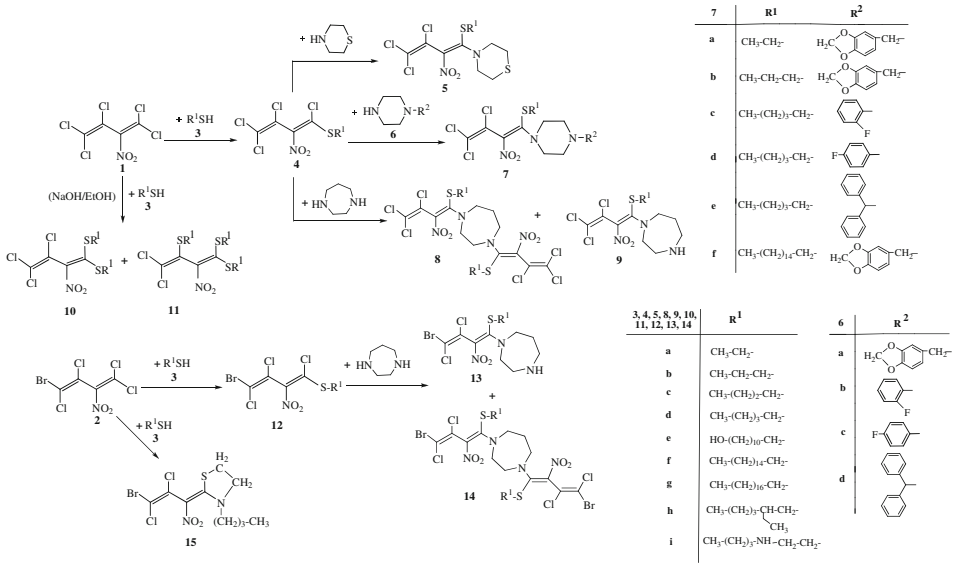
3.1 *Chemistry*

These electronically remarkable molecules can be used for a broad variety of synthetic applications since the reactions can be carried out by various methods ranging from nucleophilic vinylic substitution (S_NVinylic) pathway via the addition–elimination route and ring cleavage to addition reactions of the trichlorovinyl group activated by the nitro group which also provides regioselectivity to molecules.

Nitrodiene compounds **1** and **2** were obtained from by direct nitration of the corresponding dienes. 1, 1, 3, 4, 4-pentachloro-2-nitro-1, 3-butadiene **1** was gained from the nitration of 1, 1, 3, 4, 4-pentachloro-2-H-1, 3-butadiene with concentrated HNO_3 in about 40% yield. Nitration of a mixture of two geometric isomers of 1, 1, 3, 4-tetrachloro-4-bromo-2-nitro-1, 3-butadiene **2** with concentrated HNO_3 occurs at the dichlorovinyl group by electrophilic substitution of the H atom by the nitro group with the formation of a mixture of E- and Z-isomers of 1, 1, 3, 4-tetrachloro-4-bromo-2-nitro-1, 3-butadiene in ~40% yield.[23,24]

The reaction of pentachloro-2-nitro-1, 3-butadiene **1** with one molar equivalent of ethanethiol **3a**, propanethiol **3b**, pentanethiol **3d**, hexadecanthiol **3f**, 2-ethyl-hexanethiol **3h** in dichloromethane at room temperature furnishes (E)-1, 3, 4, 4-tetrachloro-2-nitro-1-(alkylsulphanyl)-1, 3-butadiene compounds **4a**,[14] **4b**,[25] **4d**, **4f**,[14] **4h** as a single isomer (75% yield for **4d** and 66% for **4h**). (E)-4-bromo-1, 3, 4-trichloro-2-nitro-1-(alkylsulphanyl)-1, 3-butadiene was synthesized from reaction of 4-bromo-1, 1, 3, 4-tetrachloro-2-nitrobuta-1, 3-diene **12h** (63% yield) with 2-ethyl-hexanethiol **3h** according to same method. These known (**4a**, **4b**, **4f**) and unknown (**4d**, **4h**, **12h**) mono(thio)substituted nitrobutadiene compounds were used as the starting compounds with various nuchleophilic compounds at room temperature. It is expected that mono(thio)substituted nitrobutadienes yielded products such as a mixture of E- and Z-isomers. However, in the crystal structure of S- and N, S-substituted nitrodienes reported in previous studies, it was noted that mono(thio)substituted nitrobutadienes were E-isomers and N, S-substituted nitrobutadienes were also E-isomers. As a consequence, it might be thought that the derived new nitrodiene products were probably E-isomers.[13,17,25–27] The reactions of thiomorpholine and piperazine derivatives with S-substituted-tetrachloro-2-nitro-1, 3-butadiene (**4a**, **4b**, **4d**, **4f**) gave the novel N, S-substituted-trichloro-2-nitro-1, 3-butadiene compounds (**5d**, **7a–f**). These substitution reactions proceed by addition–elimination reaction mechanism (scheme 1). First, an addition of the attacking reagent to the C,C double bond occurs, and in a second step the intermediate product is stabilized by elimination of hydrogen chloride.

Compounds **8h**, **9h**, **13h** and **14h** were obtained from the reactions of **4h** and **12h** with homopiperazine. Disubstituted butadineyl homopiperazine compounds **8h** and **14h** are interesting unsaturated compounds



Scheme 1. Synthesis pathway of polyhalo-2-nitro-1, 3-butadiene compounds.

(scheme 1). Disubstituted homopiperazine compound **8c** was earlier obtained from the reaction of mono(thio)substituted diene **4c** with homopiperazine.[18] Crystal structure of compound **8c** was determined in this study.

It is well-known that the reactions of 2-nitrodiene with some thiols follow a classical S_NVin process.[28] The 2-nitrodiene initially reacts at the terminal C-1 carbon atom to yield the product of mono(thio)substituted-2-nitrobutadienes or 1, 1-bis(thio)substituted-2-nitrobutadienes. Under more rigid conditions, a subsequent substitution of chlorine atom on C-3 carbon atom is possible. Use of three equivalents of propanthiol **3b**, 11-mercapto-1-undecanol **3e** and octadecanthiol **3g** in the presence of sodium hydroxide in ethanol at room temperature with 1, 1, 3, 4, 4-pentachloro-2-nitro-1, 3-butadiene **1** provides the di- and trisubstituted polychloro-2-nitro-1, 3-butadienes **10e**, **11e**, **11b**, **11g**. When the XRD data of tris(thio)substituted nitrodienes were investigated, it was shown that the third thiolate anion was replaced with the chlorine atom on C-3 carbon atom.[29]

The 1, 1, 3, 4-tetrachloro-4-bromo-2-nitro-1, 3-butadiene **2** reacts at the terminal C-1 carbon atom to yield the product of compound **15**. Isolation and identification proved that a cyclization reaction had taken place, yielding compound **15**.

3.2 *Discussion on NMR, IR and MS*

We realized that there were some broad peaks corresponding to the methylene protons of piperazine derivatives when we characterized the new N, S-substituted nitrodienes via the NMR technique. The piperazine protons are changing from axial to equatorial. At room temperature, there were broad peaks corresponding to piperazine protons in the ^{1}H-NMR. The ^{1}H-NMR spectra of **7a–f** showed the piperazine ring, piperazine protons are observed as broad singlets between δ 2.5–3.2 ppm and 3.5–3.8 ppm. The proton NMR data of **7a–f** showed typical ppm values and splitting patterns (AA′BB′-system of the aromatic protons) within the range of 6.6–7.5 ppm and 0.8–3.0 ppm for the methyl protons, respectively. In addition, alkyl units of **7a**, **7b**, **7e** and **7f** have been assigned by appropriate incremental shifts owing to substituted benzene derivatives.[30]

The ^{1}H-NMR spectra of **4d** showed thiomorpholine ring as triplet at δ 2.65 and broad singlet 3.4 ppm. The ^{13}C-NMR shifts of the C-1 carbon atoms of N, S-substituted-trichloro-1, 3-butadiene compound **4d** appears relatively downfield around 170 ppm, whereas the NO_2-bearing carbon atoms, C-2, each show their resonance, a broadened less intense peak, at 133 ppm. The individual C-3 and C-4 carbons provide chemical shift values around 118 ppm and 124 ppm, respectively.

In the MS[+ESI] mass spectrum of the compound **7f**, the respective molecular ion peak was observed at m/z 678 $[M]^+$ (figure 2). Also, other fragments were observed at m/z 739 $[M+Na+K]^+$, 701 $[M+Na]^+$. In MS/MS[+ESI], major fragment F_1 of compound **7f** was found at m/z 528 (figure 3). It is likely that this corresponds to the one nitronium $[NO_2]^+$ and three chlorine $[Cl]^+$ ions. The respective molecular ion peaks were observed at m/z 642 $[M–Cl]^+$,

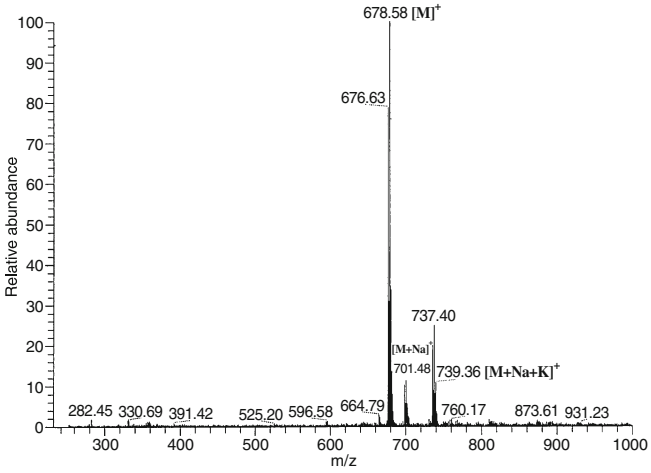


Figure 2. MS[+ESI] spectra of compound **7f**.

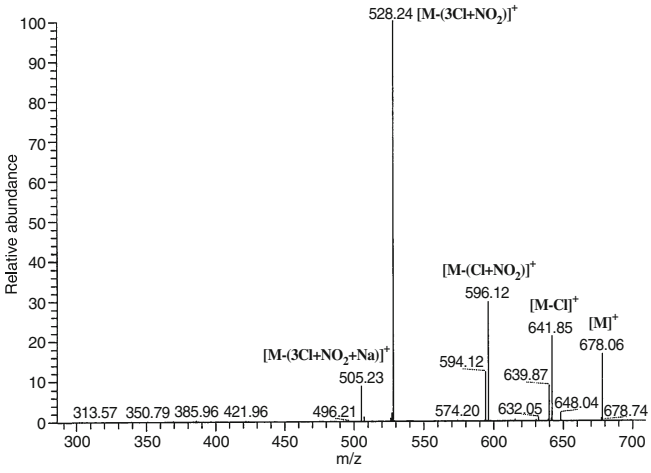


Figure 3. MS/MS[+ESI] spectra of compound **7f**.

596 $[M–(Cl+NO_2)]^+$, 505 $[M–(3Cl+NO_2+Na)]^+$ (figure 3). The results of MS[+ESI] mass spectrum of all the remaining compounds agree well with corresponding fragments in similar compounds.

Some characteristic bands in the IR spectra of all the compounds should be mentioned: The C=C stretching band is observed within the range of 1429 (asymmetric stretching) and 1696 cm^{-1} (symmetric stretching), and the NO_2 groups are observed in the range of 1255 (asymmetric stretching) and 1442 cm^{-1} (symmetric stretching). In the IR spectra of **8h** and **14h**, no band is observed in the region 3200–3450 cm^{-1}, attributable to the stretching vibration of the bonded NH group, indicating the formation of a disubstituted butadienyl homopiperazine compounds. The N–H band were observed at 3849 and 3784 cm^{-1} for compounds **9h** and **13h**, respectively.

The FT-IR spectra of **10e** and **11e** showed characteristic (–OH) bands at 3338 and 3362 cm^{-1} and there were singlet peaks corresponding to (–OH) protons at 3.0 and 3.1 ppm in the ^{1}H-NMR spectrum. The ^{13}C-NMR shifts of the butadiene unit of di(thio)substituted-butadiene compound **10e** were at 119.28, 122.13, 126.64 and 161.99 ppm; with 117.28 123.13, 155.64 and 162.99 ppm for tris(thio)substituted-butadiene compound **11e**, respectively.

3.3 *Crystal structure of disubstituted butadienyl homopiperazine compound (**6b**)*

The crystal structure of compound **8c** is shown in figure 3. The titled compound, $C_{21}H_{28}Cl_6N_4O_4S_2$, contains the expected N, S-substituted butadienyl skeleton, an alkylsulphanyl chain and homopiperazine ring. The butadiene group I has a conformation closer to cisoid than to transoid, the C1–C2–C3–C4 torsion angle being −56.0(1)°. The torsion angle of the butadiene group II is 64.0(1)°. Butadiene units are not planar as would be if the two double bonds were fully conjugated. Noncoplanar structure of the butadiene fragments of this molecule and the clear single bonds of the C2–C3 and C15–C16 bonds (1.44(1) Å and 1.42(2) Å, respectively) indicate the lack of delocalization of π-electron density in the butadiene chains, which is apparently one of the major reasons for the inertness of polychlorobutadienes and their functional derivatives with nonplanar molecular structure relative to 1, 4-addition. The C–C bond lengths within the butadiene unit are similar to those in related compounds.[31]

Homopiperazine is in a boat conformation and not planar with maximum deviation of 0.2055 Å. The boat conformation of homopiperazine ring agrees well with corresponding conformation in a similar compound.[32] Crystal structure of **8c** is the first example of disubstituted butadienyl homopiperazine compound. It is shown that the N, S-substituted polyhalogene-1, 3-butadiene compound (butadiene group I and II) were *E*-isomers, in figure 1.

4. Conclusion

With the realization of these reactions applying different nucleophiles (thiols, amines, and multifunctional nucleophiles), a highly useful and efficient synthetic methodology is developed. The significance of this project consists in the shortest possible access to highly functionalized sulphur and heterocyclic compounds from very simple precursor in a one-pot operation. Reactions of 'polyhalogenated nitrobuta-1, 3-dienes' continue to evolve, with many new possibilities reported during the last decade. In particular, we may

propose that these reactions would enable to synthesize any fundamentally desired compounds (a) in high yields and (b) efficiently (in as few steps as possible). The goal of this study was to synthesize and characterize new S-, S, S-, S, S, S-, and N,S-substituted-2-nitro-polyhalo-1, 3-butadiene compounds **4d**, **4h**, **5d**, **7a–f**, **8e**, **8–9h**, **10e**, **11b**, **11g**, **12h** and **13h**. Their structures were determined by using micro-analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR and MS. The crystal structure of compound **8c** was determined by X-ray diffraction method.

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