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The Synthesis of Novel *S*-, *S,S*-, *S,S,S*-, *S,O*-, *N,S*-Substituted Halogenobuta-1,3-dienes

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Abstract

In this work, thiosubstituted nitrodiene compounds (**3**, **4a**, **5a**,**b**, **6c**, **7a**, **7c**, **9**) were obtained from the reactions of some thiols with 2-nitropentachloro-1,3-butadiene. *N*,*S*-Substituted nitrodiene compounds (**11a**–**g**, **13**, **15**) were obtained from 2-nitropentachloro-1,3-butadiene and some amines (morpholine and piperazine derivatives). The compound **4a** was crystallized in the triclinic crystal system (space group P-1) with the unit cell parameters a = 6.6525(7) Å, b = 10.7906(5) Å, c = 10.8339(4) Å, α = 72.57(3)°, β = 84.23(4)°, γ = 75.81(3)°, V = 719.03(9) Å^3, Z = 2. The novel compounds were characterized by elemental analysis, UV-VIS, FT-IR, ^{1}H-NMR, NMR (^{13}C or APT) and mass spectroscopy.

Keywords: 1,3-Butadiene, thioethers, *N*,*S*-substituted nitrodienes, crystal structure.

1. Introduction

Due to the S_N reactivity patterns, nitro substituted polyhalogeno-1,3-butadienes have proven to be valuable synthetic precursors for the formation of a variety of polyfunctionalized bioactive heterocycles.[1–2] The thiosubstituted compounds acting as fungicides, herbicides and insecticides are often used in different biological applications.[3] It has been reported before that *S*-, *S*,*S*-, *S*,*S*,*S*-, *S*,*O*-substituted nitrodienes could be synthesized via the reactions of thiols.[4–9] From our previous studies it has been known that treatment of some mono(thio)substituted compounds with some amines (piperazine, morpholine, piperidine etc.) leads to some new *N*,*S*-substituted diene compounds.[10–11] Moreover, single crystal structures of some *N*,*S*-substituted nitrodienes were determined before.[12–13] In this study, we have determined the single crystal structure of **4a**. Furthermore, piperazine compounds are important substances in clinical chemistry.[14–15] As a ligand the 2-mercaptophenol has been shown to be highly versatile, which ligates as well as chelates and bridges to metal atoms in at least eight different coordination modes.[16] The goal of this study was to synthesize and characterize new thiosubstituted 1,3-butadiene compounds.

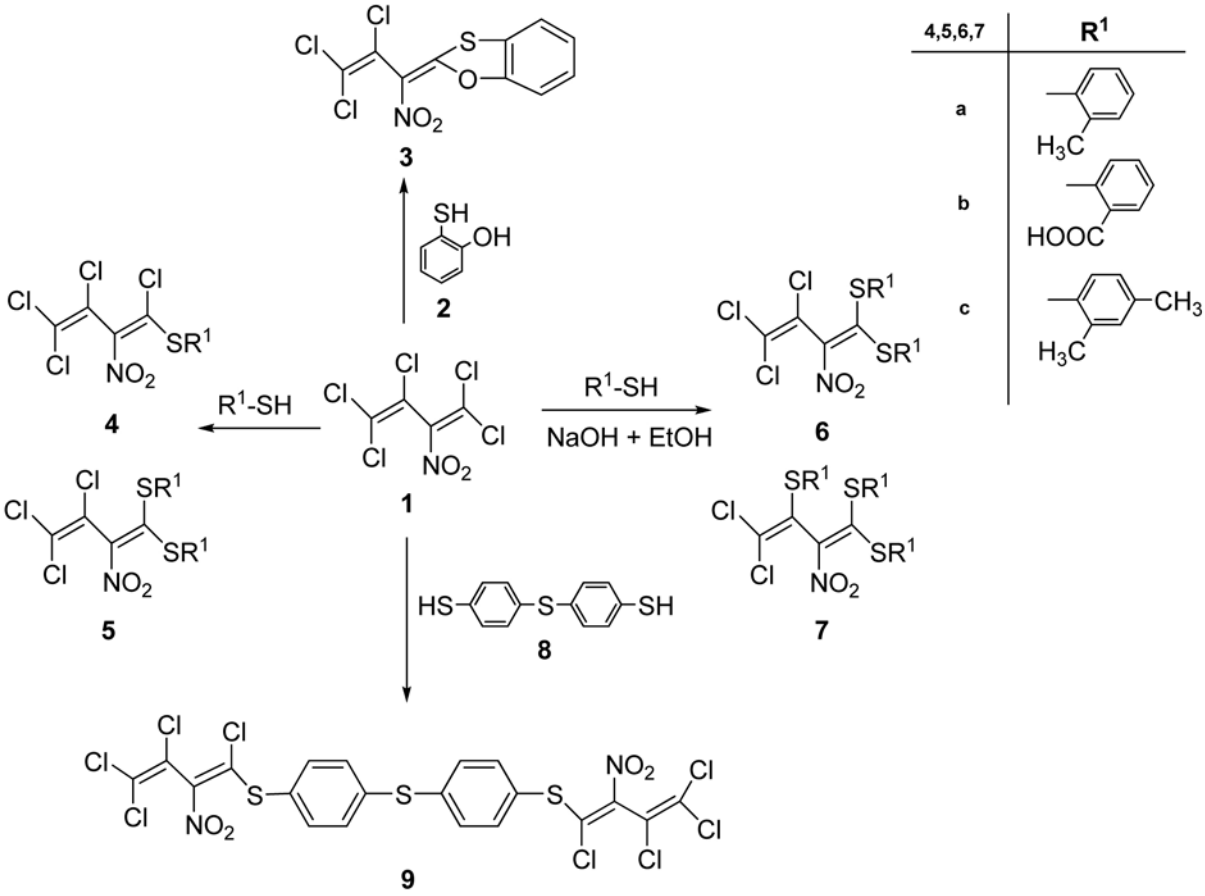
2. Experimental Section

2. 1. General

Melting points were measured on a Buchi B-540 melting point apparatus and are uncorrected. Infrared (FT-IR) spectra were recorded using Shimadzu FTIR-8101 spectrometer. The samples were pressed in KBr pellets. Elemental analyses were performed with Carlo Erba 1106 Elemental analyser. UV spectra were recorded with UV-VIS Spectrophotometer TU-1901. ^{1}H and ^{13}C or APT NMR spectra were recorded on Varian UNITY INOVA operating at 500 MHz. Mass spectrum were obtained on a Thermo Advantage MAX LC/MS/MS spectrometer according to APCI or ESI. Crystal structure of **4a** was determined on Rigaku R-Axis Rapid-S X-Ray Single Crystal Diffractometer. Products were isolated by column chromatography on silica gel (Fluka Silika gel 60, particle size 63–200 μm). TLC plates were of silica 60F_{254} (Merck, Darmstadt), detection with ultraviolet light (254 nm).

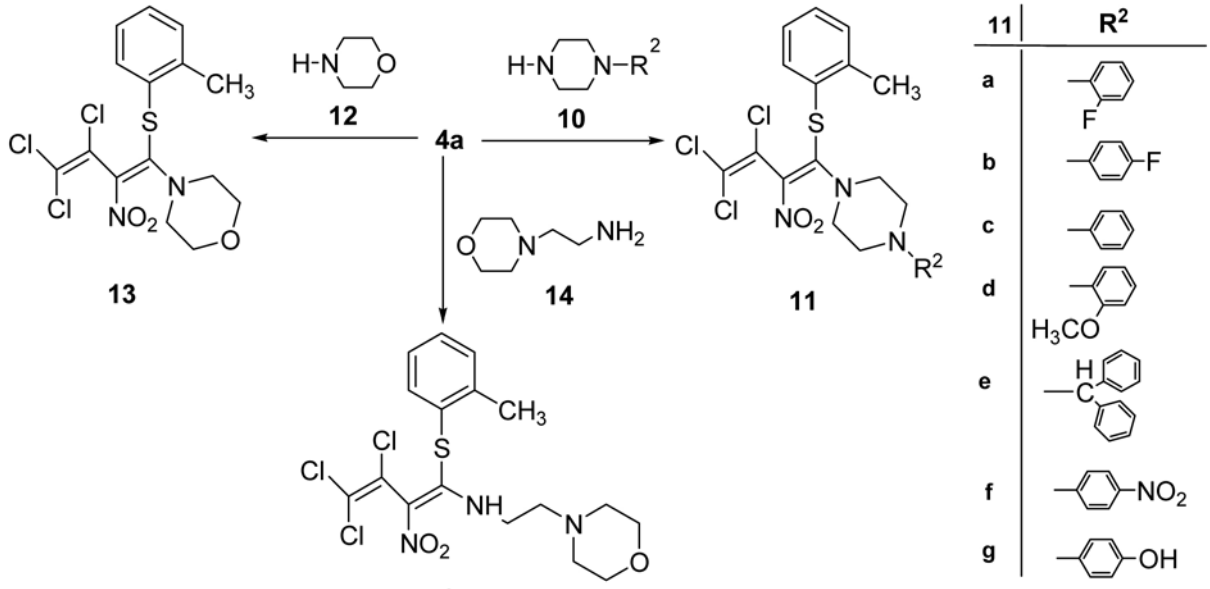
2. 2. Synthesis

S,*O*-Substituted nitrodiene compound **3** was obtained from the reactions of 2-nitropentachloro-1,3-butadiene with 2-mercaptophenol. The reaction of 2-nitropentachloro-1,3-bu-



Scheme 1. Synthesis of compounds **3**, **4a**, **5a**,**b**, **6c**, **7a**, **7c**, **9**

tadiene with 2-methyl benzenethiol yielded **4a**. The crystal structure of this novel compound was characterized by using X-ray diffraction. Disubstituted nitrodiene compounds **5a**,**b** were obtained from the reactions of 2-nitropentachloro-1,3-butadiene with thiols. Also, the compounds **6c**, **7a** and **7c** were synthesized in the presence of NaOH and EtOH from the reactions of 2-nitropentachloro-1,3-butadiene with thiols. These reactions are showed in Scheme 1.



Scheme 2. Synthesis of compounds **11a–g**, **13**, **15**

N,S-Substituted diene compounds **11a**–**g**, **13** and **15** were prepared by the reactions of **4a** with amines (piperazine, morpholine, etc.) in the presence of dichloromethane. The novel *N,S*-substituted compounds are showed in Scheme 2. These novel compounds were formed by an addition-elimination reaction sequence and all products obtained were found to be stable. The structures of the new nitrodine compounds are in accordance with the analytical and spectroscopic data as given in the experimental part.

2. 3. Preparation of *S*-, *S,S*-, *S,S,S*-, *S,O*-Substituted Nitrobutadiene Compounds

2. 3. 1. General Procedure for 1

Equimolar amounts of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene and various thiols were stirred for 24 h at room temperature. Chloroform was added to the reaction mixture and the organic layer was washed with water (4 × 30 mL) and dried with Na_2SO_4. After filtering, the solvent was evaporated and the residue was purified by column choromatography on silicagel. (Scheme 1)

2. 3. 2. General Procedure for 2

Equimolar amounts of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene and thiols were stirred in a mixture of EtOH (30 mL) and aqueous solution of NaOH (1.2 g NaOH and 8 mL water) for 2 h at room temperature. Chloroform was added to the reaction mixture to form the organic layer. Then, the organic layer was washed with water (4 × 30 mL) and dried with Na_2SO_4. After filtering, the solvent was evaporated and the residue was purified by column choromatography on silicagel. (Scheme 1)

2. 4. Preparation of *N,S*-Substituted Nitrobutadiene Compounds

2. 4. 1. General Procedure for 3

Equimolar amounts of *S*-substituted polyhalonitrodienes and amine derivatives were stirred in CH_2Cl_2 for 2 h at room temperature. Additional chloroform was added to the reaction mixture and the organic layer was washed with water (4 × 30 mL) and dried with Na_2SO_4. After filtering, the solvent was evaporated and the residue was purified by column choromatography on silicagel. (Scheme 2)

2. 5. Experimental

Synthesis of 3,4,4-Trichloro-1-[enzo(1,3-oxathia)]-2-nitro-1,3-butadiene (3). Compound **3** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2-mercaptophenol (**2**) (0.93 g, 7.37 mmol) according to the general procedure 1.

3: Yellow crystals, mp: 132–133 °C. Yield: 1.06 g (45%). R*f* (petroleum ether): 0.35. IR (KBr, cm^{-1}): ν 3096 (C–H_{arom}), 1600, 1618 (C=C), 1294, 1547 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 240.88 (4.76), 374.52 (4.77) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 7.42 (t, *J* = 7.5 Hz, H, H_{arom}), 7.50 (t, *J* = 8.1 Hz, H, H_{arom}), 7.56 (d, *J* = 7.8 Hz, H, H_{arom}), 7.66 (d, *J* = 7.5 Hz, H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 110.82, 111.95, 121.44, 122.54, 125.43, 126.74, 127.67, 132.23, 152.11, 160.87. MS [ESI+]: *m/z* 326 $[M+H]^+$. Anal. Calcd for $C_{10}H_4Cl_3NO_3S$ (*M* = 324.57 g/mol): C, 37.01; H, 1.24; N, 4.32; S, 9.88. Found: C, 36.74; H, 1.35; N, 4.13; S, 9.65.

Synthesis of 2-Nitro-1,3,4,4-tetrachloro-1-(2-methylphenylthio)-1,3-butadiene (4a). Compound **4a** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2-methylthiophenol (0.91 g, 7.36 mmol) according to the general procedure 1.

4a: Yellow crystals, mp: 119–120 °C. Yield: 1.28 g (49%). R*f* [petroleum ether/$CHCl_3$ (1:1)]: 0.46. IR (KBr, cm^{-1}): ν 3056 (C–H_{arom}), 2921, 2986 (C–H), 1599 (C=C), 1304, 1533 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 240.88 (4.1), 344.27 (4.2) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.43 (t, 3H, CH_3), 7.29–7.36 (m, 2H, H_{arom}), 7.44–7.52 (m, 2H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.5 (CH_3), 120.35, 127.36, 127.37, 127.76, 142.35, 156.81 (C_{butad}, C_{arom}), 126.26, 130.26, 131.04, 135.87 (CH_{arom}). MS [APCI+]: *m/z* 277 $[M–Cl–NO_2]^+$, 278 $[M+H]^+$. Anal. Calcd for $C_{11}H_7Cl_4NO_2S$ (*M* = 359.06 g/mol): C, 36.80; H, 1.97; N, 3.90; S, 8.93. Found: C, 36.49; H, 1.72; N, 3.63; S, 9.14.

Synthesis of 1,1-Bis(2-methylphenylthio)-3,4,4-trichloro-2-nitro-1,3-butadiene (5a). Compound **5a** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2-methylthiophenol (0.91 g, 7.36 mmol) according to the general procedure 1.

5a: Orange solid, mp: 124–125 °C. Yield: 0.72 g (23%). R*f* [petroleum ether/$CHCl_3$ (1:1)]: 0.51. IR (KBr, cm^{-1}): ν 3061 (C–H_{arom}), 2854, 2925 (C–H), 1296, 1518 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 239.35 (4.1), 259.92 (4.1), 366.70 (3.8) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.48 (s, 6H,CH_3), 6.97–7.56 (m, 8H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.86, 19.94, 125.39, 125.77, 125.88, 126.67, 128.06, 128.14, 129.45, 129.51, 129.68, 129.82, 130.21, 130.56, 130.88, 131.53, 154.78, 159.0. MS [ESI+]: *m/z* 448 $[M+H]^+$. Anal. Calcd for $C_{18}H_{14}Cl_3NO_2S_2$ (*M* = 446.80 g/mol): C, 48.39; H, 3.16; N, 3.13; S, 14.35. Found: C, 48.21; H, 3.34; N, 2.87; S, 14.09.

Synthesis of 1,1-Bis(2-carboxyphenylthio)-3,4,4-trichloro-2-nitro-1,3-butadiene (5b). Compound **5b** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pen-

tachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2-mercaptosalicylicacid (1.13 g, 7.36 mmol) according to the general procedure 1.

5b: Yellow solid, mp: 206–207 °C. Yield: 1.89 g (51%). R*f* ($CHCl_3$): 0.50. IR (KBr, cm^{-1}): ν 2871, 2975, 3064 (C–H_{arom}), 3384 (COOH), 1681 (C=O), 1269, 1416 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 239.16 (3), 262.64 (2.8) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 7.30–7.33 (t, *J* = 8.0 Hz, 2H, H_{arom}), 7.51–7.54 (t, *J* = 8.2 Hz, 2H, H_{arom}), 7.61 (d, *J* = 8.3 Hz, 2H, H_{arom}), 8.01 (d, *J* = 7.8 Hz, 2H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 125.63, 126.53, 129.60, 132.15, 133.60, 139.60, 168.52. MS [ESI+]: *m/z* 507 $[M+H]^+$. Anal. Calcd for $C_{18}H_{10}Cl_3NO_6S_2$ (*M* = 506.77 g/mol): C, 42.66; H, 1.99; N, 2.76; S, 12.65. Found: C, 42.41; H, 1.72; N, 2.47; S, 12.96.

Synthesis of 1,1-Bis(2,4-dimethylphenylthio)-3,4,4-trichloro-2-nitro-1,3-butadiene (6c). Compound **6c** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2,4-dimethylthiophenol (1.01 g, 7.36 mmol) according to the general procedure 2.

6c: Yellow crystal, mp: 132–133 °C. Yield: 2.01 g (58%). R*f* [petroleum ether/$CHCl_3$ (1:1)]: 0.54. IR (KBr, cm^{-1}): ν 3005 (C–H_{arom}), 2730, 2920, 2954 (C–H), 1564, 1595 (C=C), 1281, 1512 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 239.51 (4.2), 263.32 (3.9), 384.38 (3.7) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.48 (s, 12H, CH_3), 6.79–7.00 (m, 6H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.01, 19.35, 20.06, 20.19 (CH_3), 121.66, 125.21, 126.23, 126.25, 126.46, 126.64, 127.13, 130.17, 130.26, 130.47, 131.98, 134.87, 138.64, 139.23, 140.04, 141.32. MS [ESI+]: *m/z* 476 $[M+H]^+$. Anal. Calcd for $C_{20}H_{18}Cl_3NO_2S_2$ (*M* = 474.85 g/mol): C, 50.59; H, 3.82; N, 2.95; S, 13.51. Found: C, 50.35; H, 4.11; N, 2.68; S, 13.32.

Synthesis of 1,1,4-Tris(2-methylphenylthio)-3,4-dichloro-2-nitro-1,3-butadiene (7a). Compound **7a** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2-methylthiophenol (1.37 g, 11.0 mmol) according to the general procedure 2.

7a: Orange solid, mp: 124–125 °C. Yield: 2.26 g (58%). R*f* ($CHCl_3$): 0.51. IR (KBr, cm^{-1}): ν 3049, 2974, 2937 (C–H_{arom}), 2738, 2676, 2491 (C–H), 1593 (C=C), 1286, 1537 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 241.18 (3.1), 260.76 (3), 362.43 (2.9) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 1.79 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 6.82–7.20 (m, 10H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 20.28, 20.69 (CH_3), 122.64, 128.62, 129.76, 131.06, 140.29, 142.72 (C_{butad}, C_{arom}), 126.64, 127.12, 129.31, 130.68, 130.76, 130.93, 132.75, 136.04 (CH_{arom}). MS [ESI–]: *m/z* 533 $[M–H]^+$. Anal. Calcd for $C_{25}H_{21}Cl_2NO_2S_3$ (*M* = 534.54 g/mol): C, 56.17; H, 3.96; N, 2.62; S, 18.0. Found: C, 55.86 ; H, 3.68; N, 2.86; S, 18.29.

Synthesis of 1,1,4-Tris(2,4-dimethylphenylthio)-3,4-dichloro-2-nitro-1,3-butadiene (7c). Compound **7c** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 2,4-dimethylthiophenol (1.52 g, 11 mmol) according to the general procedure 2.

7c: Yellow solid, mp: 133–134 °C. Yield: 2.44 g (58%). R*f* [petroleum ether/$CHCl_3$ (1:1)]: 0.38. IR (KBr, cm^{-1}): ν 3005 (C–H_{arom}), 2730, 2920, 2954 (C–H), 1564, 1595 (C=C), 1281, 1512 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 244.58 (2.8), 272.75 (2.6), 372.9 (2.8) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 1.81 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.21 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 6.72–6.92 (m, 9H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 20.27, 20.61, 21.35, 21.48 (CH_3), 122.88, 126.38, 127.44, 127.51, 127.89, 128.36, 129.04, 131.5, 131.72, 133.19, 136.11, 139.81, 139.89, 140.45, 141.32, 142.56. MS [ESI+]: *m/z* 576 $[M–H]^+$. Anal. Calcd for $C_{28}H_{27}Cl_2NO_2S_3$ (*M* = 576.62 g/mol): C, 58.32; H, 4.72; N, 2.43; S, 16.68. Found: C, 58.06; H, 4.42; N, 2.26; S, 16.94.

Synthesis of 1-[(1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl)sulfanyl]-4-([4-[(1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl)sulfanyl]phenyl}sulfanyl)benzene (9). Compound **9** was synthesized from the reaction of 2-nitro-1,1,3,4,4-pentachloro-1,3-butadiene (**1**) (2.00 g, 7.37 mmol) with 4,4'-thiobisbenzenthiol (**8**) (1.84 g, 7.37 mmol) according to the general procedure 1.

9: Yellow solid, mp: 105–106 °C. Yield: 2.26 g (43%). R*f* [petroleum ether/$CHCl_3$ (1:1)]: 0.47. IR (KBr, cm^{-1}): ν 3050 , 3069 (C–H_{arom}), 1639 (C=C), 1472, 1565 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 255 (4.3) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 7.04–7.06 (d, 4H, H_{arom}), 7.17–7.19 (d, 4H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 127.49, 129.50, 130.54, 131.13, 134.67, 135.3. MS [ESI+]: *m/z* 721 $[M+H]^+$. Anal. Calcd for $C_{20}H_8Cl_8N_2O_4S_3$ (*M* = 720.11 g/mol): C, 33.36; H, 1.12; N, 3.89; S, 13.36. Found: C, 33.12; H, 1.41; N, 3.63; S, 13.15.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(2-flourophenyl)piperazine (11a). Compound **11a** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(2-flourophenyl)piperazine (0.25 g, 1.38 mmol) according to the general procedure 3.

11a: Yellow crystals, mp: 181–182 °C. Yield: 0.39 g (55%). R*f* ($CHCl_3$): 0.37. IR (KBr, cm^{-1}): ν 3066 (C–H_{arom}), 2827, 2922 (C–H), 1595, 1610 (C=C), 1271, 1542 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 242.24 (2.9), 282.37 (2.5), 389.39 (2.8) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.37 (s, H, CH_3), 2.85 (brs, 4H,

H_{piper}), 3.34–3.74 (m, 4H, H_{piper}), 6.71–7.34 (m, 9H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.72, 48.49, 52.23, 115.31, 115.48, 118.28, 122.69, 123.60, 126.68, 128.87, 129.07, 130.55, 133.15, 134.80, 137.49, 137.56, 153.73, 155.69, 165.99. MS [ESI+]: *m/z* 526 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{19}Cl_3FN_3O_2S$ (*M* = 502.82 g/mol): C, 50.16; H, 3.81; N, 8.36; S, 6.38. Found: C, 49.93; H, 3.51; N, 8.09; S, 6.12.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(4-flourophenyl)piperazine (11b). Compound **11b** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(4-flourophenyl)piperazine (0.25 g, 1.38 mmol) according to the general procedure 3.

11b: Yellow crystals, mp: 146–147 °C. Yield: 0.42 g (60%). R*f* (EtAc): 0.39. IR (KBr, cm^{-1}): ν 3066 (C–H_{arom}), 2827, 2922 (C–H), 1595, 1610 (C=C), 1271, 1542 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 245.89 (3.4), 293.05 (2.7), 389.13 (3.2) nm; ^1H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.36 (s, 3H, CH_3), 2.84 (brs, 4H, H_{piper}), 3.48–3.72 (m, 4H, H_{piper}), 6.69–7.32 (m, 8H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.73 (CH_3), 48.56, 51.98 (C_{piper}), 118.77, 124.2, 125.67, 139.04, 145.66, 155.89, 157.80, 166.07 (C_{butad}, $C_{arom.}$), 114.72, 114.90, 117.64, 117.70, 126.69, 129.12, 130.56, 133.16 ($CH_{arom.}$). MS [ESI+]: *m/z* 504 $[M+H]^+$. Anal. Calcd for $C_{21}H_{19}Cl_3FN_3O_2S$ (*M* = 502.82 g/mol): C, 50.16; H, 3.81; N, 8.36; S, 6.38. Found: C, 49.93; H, 3.63; N, 8.12; S, 6.15.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(1-phenyl)piperazine (11c). Compound **11c** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-phenylpiperazine (0.22 g, 1.39 mmol) according to the general procedure 3.

11c: Red solid, mp: 146–147 °C. Yield: 0.28 g (41%). R*f* [$CHCl_3$/EtAc (1:1)]: 0.42. IR (KBr, cm^{-1}): ν 3062, 3042 (C–$H_{arom.}$), 2971, 2915, 2842 (C–H), 1581, 1618 (C=C), 1272, 1524 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 243.17 (1.7), 387.14 (1.7) nm; ^1H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.37 (s, 3H, CH_3), 2.95 (brs, 4H, H_{piper}), 3.50–3.74 (m, 4H, H_{piper}), 6.70–7.33 (m, 9H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.74 (CH_3), 47.61, 51.95 (C_{piper}), 116.22, 124.91, 126.40, 128.27, 139.01, 141.85, 148.98 (C_{butad}, C_{arom}), 115.63, 120.03, 126.69, 128.33, 129.12, 130.54, 133.14 (CH_{arom}). MS [ESI+]: *m/z* 508 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{20}Cl_3N_3O_2S$ (*M* = 484.83 g/mol): C, 52.02; H, 4.16; N, 8.67; S, 6.61. Found: C, 51.83; H, 3.89; N, 8.82; S, 6.82.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(2-metoxyphenyl)piperazine (11d). Compound **11d** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(2-metoxyphenyl)piperazine (0.26 g, 1.39 mmol) according to the general procedure 3.

11d: Yellow crystals, mp: 174–175 °C. Yield: 0.44 g (61%). R*f* (EtAc): 0.43. IR (KBr, cm^{-1}): ν 3011, 3062 (C–$H_{arom.}$), 2823, 2928, 2967, (C–H), 1580 (C=C), 1268, 1531 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 246.87 (3.1), 285.84 (2.8), 389.56 (3) nm; ^1H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.37 (s, 3H, CH_3), 2.90 (brs, 4H, H_{piper}), 3.53 (brs, 4H, H_{piper}), 3.82 (s, 3H, OCH_3), 6.66–6.67 (d, *J* = 7.3, H, H_{arom}), 6.78–6.84 (m, 2H, H_{arom}), 6.94–6.97 (t, *J* = 7.8, H, H_{arom}), 7.14–7.25 (m, 3H, H_{arom}), 7.33–7.34 (d, *J* = 7.8, H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 20.98, 49.78, 53.77, 55.72, 122.0, 126.1, 130.2, 133.6, 135.3, 139.94, 140.25, 152.48. MS [ESI+]: *m/z* 516 $[M+H]^+$. Anal. Calcd for $C_{22}H_{22}Cl_3N_3O_3S$ (*M* = 514.86 g/mol): C, 51.32; H, 4.31; N, 8.16; S, 6.23. Found: C, 51.14; H, 4.54; N, 7.92; S, 6.45.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(1-diphenylmethyl)piperazine (11e). Compound **11e** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(dimethylphenyl)piperazine (0.35 g, 1.39 mmol) according to the general procedure 3.

11e: Yellow crystals, mp: 181–182 °C. Yield: 0.44 g (55%). R*f* ($CHCl_3$): 0.38. IR (KBr, cm^{-1}): ν 3019, 3059 (C–$H_{arom.}$), 2821, 2911, 2972 (C–H), 1586 (C=C), 1282, 1530 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 245.24 (3.5), 296.98 (3.1), 389.59 (3.6) nm; ^1H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.29 (s, 3H, CH_3), 3.36 (brs, 4H, H_{piper}), 3.63 (brs, 4H, H_{piper}), 4.09 (s, H, CH), 7.08–7.27 (m, 14H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.66, 49.8 74.33, 126.3, 126.7, 128.91, 131.5, 138.9, 140.37, 142. MS [ESI+]: *m/z* 576 $[M+H]^+$. Anal. Calcd for $C_{28}H_{26}Cl_3N_3O_2S$ (*M* = 574.95 g/mol): C, 58.49; H, 4.56; N, 7.31; S, 5.58. Found: C, 58.28; H, 4.27; N, 7.05; S, 5.81.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(4-nitrophenyl)piperazine (11f). Compound **11f** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(4-nitrophenyl)piperazine (0.28 g, 1.39 mmol) according to the general procedure 3.

11f: Red solid, mp: 189–190 °C. Yield: 0.39 g (53%). R*f* [$CHCl_3$/EtAc (1:1)]: 0.45. IR (KBr, cm^{-1}): ν 3436 (C–H_{arom}), 2870 (C–H), 1598 (Ar–NO_2), 1285, 1513 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 245.5 (2.4), 377.08 (3.1) nm; ^1H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.49 (s, 3H, CH_3), 3.21 (brs, 4H, H_{piper}), 3.53–3.69 (m, 4H, H_{piper}), 6.67–6.69 (d, *J* = 7.32, H, H_{arom}), 7.15–7.33 (m, 5H, H_{arom}), 8.05–8.08 (m, 2H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 20.97 (CH_3), 46.31, 52.10

(C_{piper}), 113.44, 126.16, 128.0, 130.5, 131.91, 134.10, 134.84 (CH_{arom}), 126.58, 129.84, 139.96, 140.23, 153.87, 184.30, 191.09 (C_{butad}, C_{arom}). MS [ESI+]: *m/z* 553 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{19}Cl_3N_4O_4S$ (*M* = 529.82 g/mol): C, 47.61; H, 3.61; N, 10.57; S, 6.05. Found: C, 47.42; H, 3.83; N, 10.31; S, 5.87.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(4-hidroxyphenyl)piperazine (11g). Compound **11g** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(4-hidroxyphenyl)piperazine (0.24 g, 1.39 mmol) according to the general procedure 3.

11g: Yellow solid, mp: 203–204 °C. Yield: 0.31 g (44%). R*f* [$CHCl_3$/EtAc (1:1)]: 0.41. IR (KBr, cm^{-1}): ν 3344 (O–H), 2918 ($CH_{arom.}$), 2815 (C–H) 1214, 1511 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 246.83 (2.5), 274.06 (2), 388.72 (2.5) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.37 (s, 3H, CH_3), 3.50 (brs, 4H, H_{piper}), 3.75 (brs, 4H, H_{piper}), 6.68 (s, H, OH), 7.15–7.33 (m, 8H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.73, 49.21, 52.17, 108.78, 115.04, 118.28, 126.68, 128.72, 128.82, 129.02, 129.08, 133.18, 139.02. MS [ESI+]: *m/z* 500 $[M–H]^+$. Anal. Calcd for $C_{21}H_{20}Cl_3N_3O_3S$ (*M* = 500.83 g/mol): C, 50.36; H, 4.03 ; N, 8.39; S, 6.40. Found: C, 50.13; H, 3.87; N, 8.13; S, 6.15.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-morpholine (13). Compound **13** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with *N*-morpholine (**12**) (0.12 g, 1.39 mmol) according to the general procedure 3.

13: Yellow crystals, mp: 138–139 °C. Yield: 0.36 g (63%). R*f* (EtAc): 0.53. IR (KBr, cm^{-1}): ν 3061 (Ar–CH), 2966, 2856, 2923 (C–H), 1275, 1538 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 245.84 (3.6), 293.38 (3.1), 389.26 (3.6) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 2.35 (s, 3H, CH_3), 3.20–3.42 (m, 4H, H_{morp}), 3.55–3.71 (m, 4H, H_{morp}), 7.17–7.33 (m, 4H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 19.69 (CH_3), 52.40, 64.52 (C_{morp}), 119.35, 126.80, 128.85, 130.01, 134.01, 140.16 (C_{butad}, C_{arom}), 126.70, 129.14, 130.58, 133 (CH_{arom}). MS: [ESI+]: *m/z* 411 $[M+H]^+$. Anal. Calcd for $C_{15}H_{15}Cl_3N_2O_3S$ (*M* = 409.72 g/mol): C, 43.97; H, 3.69; N, 6.84; S, 7.83. Found: C, 43.83; H, 3.45; N, 6.59; S, 8.01.

Synthesis of 1-[2-Nitro-3,4,4-trichloro-1-(2-methylphenylthio)-1,3-butadienyl]-4-(2-aminoethyl)morpholine (15). Compound **15** was synthesized from the reaction of 2-methylphenyl-1,3,4,4-tetrachloro-2-nitrobuta-1,3-dien-1-yl sulfide (**4a**) (0.5 g, 1.39 mmol) with 1-(2-aminoethyl)morpholine (**14**) (0.18 g, 1.39 mmol) according to the general procedure 3.

15: Yellow crystals, mp: 121–122 °C. Yield: 0.32 g (52%). R*f* (EtAc): 0.43. IR (KBr, cm^{-1}): ν 2923 (Ar–CH), 3335 (N–H), 2853 (C–H), 1539, 1588 (C=C), 1275, 1465 (C–NO_2). UV-VIS ($CHCl_3$): λ_{max} (log ε) 243.93 (3), 345.41 (3.2) nm; ^{1}H NMR (499.74 MHz, $CDCl_3$, ppm): δ 1.18 (s, 3H, CH_3), 2.35 (s, 2H, CH_2), 3.35 (brs, H, NH), 3.37–3.48 (m, 4H, H_{morp}), 3.52–3.66 (m, 4H, H_{morp}), 7.01–7.46 (m, 4H, H_{arom}). APT NMR (125.66 MHz, $CDCl_3$, ppm): δ 18.98 (CH_2), 28.69 (CH_3), 52.37, 64.54 (C_{morp}), 125.66, 126.70, 130.58, 131.83, 133.01, 137.04 (C_{butad}, C_{arom}), 134.44, 136.46, 138.93 (CH_{arom}). MS [ESI+]: *m/z* 393 $[M–NO_2]^+$. Anal. Calcd for $C_{16}H_{18}Cl_3N_3O_3S$ (*M* = 438.76 g/mol): C, 43.80; H, 4.14; N, 9.58; S, 7.31. Found: C, 43.65; H, 3.91; N, 9.41; S, 7.12.

3. X-Ray Crystal Structure Determination

All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation λ = 0.71073 Å. The data were collected at a temperature of 20 °C to a maximum 2è value of 60.2°. Crystallographic data for **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-No 821368.[17] Yellow crystals of **4a** suitable for X-ray diffraction analysis were obtained by slow evaporation of ethanol at room temperature. Structure solution was by direct methods SIR92[18] and refinement was by full-matrix least-squares on F using the CRYSTALS[19] program package. All non-hydrogen atoms were refined using the riding model. All calculations were performed using the Crystal Structure Crystallographic Software Package.[20] The diagram of **4a** by using ORTEP III[21] program with 30% probability displacement ellipsoide is given in Fig.1. The molecule packing diagram for **4a** is shown in Fig. 2 as a projection along the *b* axis. The molecular structure of the title compound is shown in Table 1 and selected atom distances and angles of **4a** are given in Table 2.

4. Results and Discussion

In the IR spectrum of **3** there were no typical absorption bands at about 3200–3400 cm^{-1} (as a broad peak) and 2550–2560 cm^{-1} regions corresponding to OH and SH groups, respectively. Moreover, the mass spectrum of **3** showed the protonated molecular ion peak at *m/z* 326 $[M+H]^+$. Spectroscopic evidence for the compound **3** proved the products to be of cyclyc thioether structure. In the APT-NMR spectrum of **4a**, methyl carbon atom signals have appeared at δ 19.5 ppm and the protons of methyl group have been observed as a triplet at δ 2.43 ppm. The FT-IR spectrum of **5b** showed characteristic absorption as a broad peak at 3384 cm^{-1}. In the mass spectrum of **5b** a protonated molecular ion peak has been noticed at *m/z*

507 [M+H]. The protonated molecular ion peak of **6c** was observed at *m/z* 476 in the mass spectrum. In the ^{1}H-NMR spectrum of tris thiosubstituted nitrodiene compound **7a** was aromatic protons at δ 6.82–7.20 ppm were observed as a multiplet. In UV-VIS spectrum of **9** maximum absorption was observed at 255 nm. In the ^{1}H-NMR spectrum of compound **9** of the aromatic protons two dublets located at δ 7.04–7.06 and 7.17–7.19 ppm were observed. In the ^{13}C-NMR of the compound **11d** methoxy group appeared at δ 55.72 ppm. The same methoxy group in the ^{1}H-NMR spectrum of **11d** was observed at δ 3.82 ppm as a singlet. In the ^{1}H-NMR spectrum of the compound **11e** CH group proton appeared at δ 4.09 ppm as a singlet; accordingly in the ^{13}C-NMR the same group showed a signal at δ 74.33 ppm. The FT-IR spectrum of the compound **11g** showed a characteristic band at 3344 cm^{-1}.

While NH group was observed in the ^{1}H-NMR spectrum of compound **15** as a broad singlet at δ 3.35 ppm, the IR band was at 3335 cm^{-1} supporting the accuracy of the structure **15**. Moreover, the molecular ion peak in ESI+ MS for **15** was obtained at *m/z* 439. The loss of nitro group fragment from the structure of **15** was showed by the mass peak at *m/z* 393.

The novel compounds which were synthesized have been purified with column chromatography and their structures clarified by microanalysis and spectroscopic methods (IR, ^{1}H-NMR, ^{13}C or APT NMR, MS and UV/VIS).

In our previous study the monothiosubstituted nitrodiene compound 1,3,4,4-tetrachloro-4-(4-chlorophenylsulfanyl)-2-nitrobuta-1,3-diene crystallized in the triclinic crystal system.[22] In this study the novel compound **4a** also crystallized in the triclinic crystal system (space group P-1) with the unit cell parameters a = 6.6525(7) Å, b = 10.7906(5) Å , c = 10.8339(4) Å , α = 72.57(3)°, β = 84.23(4)°, γ = 75.81(3)°, V = 719.03(9) Å^3, Z = 2.

The torsion angles and geometric structure of compounds 1,3,4,4-tetrachloro-4-(4-chlorophenylsulfanyl)-2-nitrobuta-1,3-diene[22] and the novel compound **4a** are similar to each others (in ORTEP III). The crystallographic and structure refinement data for **4a** are summarized in Table 1. In the butadien skeleton, bond lenght C1–C2 is 1.305(4) Å, C2–C3 1.467(3) Å and C3–C4 1.356(3) Å,

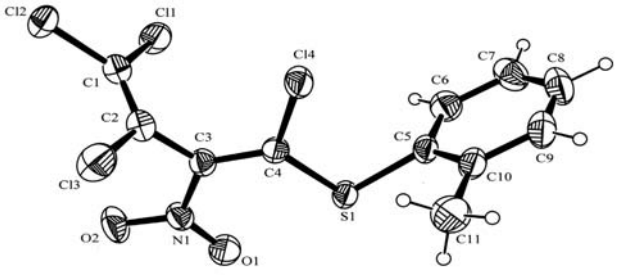


Figure 1. The molecular structure of compound **4a** (ORTEP III). Displacement ellipsoids are shown at the 30% probability level.

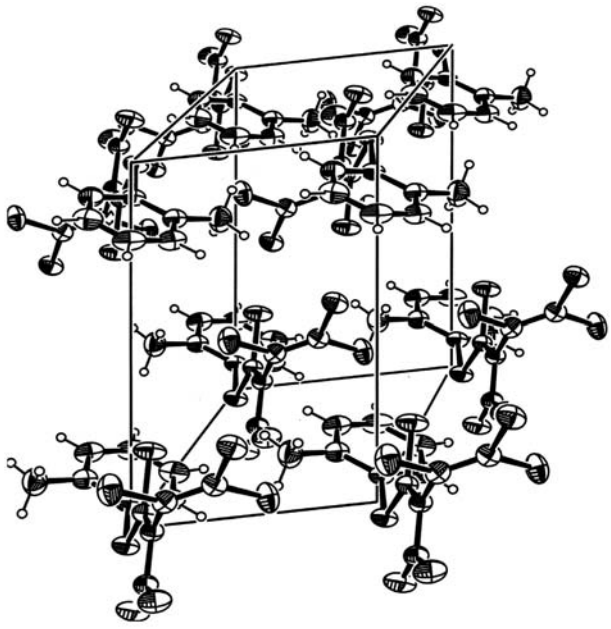


Figure 2. Packing diagram of **4a**; molecular overlap view from the *b* axis.

Table 1. Crystallographic data and structure refinement for **4a**

Formula	$C_{11}H_7Cl_4NO_2S$
Formula Weight	359.05
Crystal system	Triclinic
Space Group	P-1
Lattice Parameters	a = 6.6525(7) Å, b =10.7906(5) Å, c =10.8339(4) Å, α = 72.57(3)°, β = 84.23(4)°, γ = 75.81(3)°
V [Å^3]	719.03(9)
Z	2
D_{calc} (g/cm^3)	1.658 g/cm^3
μ [mm^{-1}]	0.961
F_{000}	360.00
Index ranges	$-7 \le h \le 7$, $-12 \le k \le 12$, $-12 \le l \le 12$
Reflections collected	39062
Independent reflections	2547 (R_{int} = 0.029)
Goodness-of-fit on F	1.014
Final R indices [$I > 3\sigma(I)$]	R = 0.039, wR = 0.053
Largest diff. peak and hole	0.57 and –0.31 e.Å^{-3}

Table 2. Selected bond lengths [Å] and angles [°] with e.s.d in parentheses for **4a**

Atom	Distance [Å]	Atom	Angle [°]
Cl(4)–C(4)	1.720(3)	C(5)–S(1)–C(4)	104.2(1)
Cl(2)–C(1)	1.727(2)	C(3)–N(1)–O(1)	119.3(2)
S(1)–C(4)	1.731(2)	C(4)–C(3)–N(1)	113.9(2)
O(2)–N(1)	1.228(3)	C(10)–C(5)–S(1)	121.3(2)
O(1)–N(1)	1.217(3)	Cl(3)–C(2)–C(3)	117.0(2)
C(1)–C(2)	1.305(4)	C(6)–C(5)–S(1)	116.7(2)
C(8)–C(9)	1.355(5)	O(2)–N(1)–O(1)	123.2(3)

respectively, typical of C–C bonds. The torsion angles of **4a** were 92.6(2)° for C4–S1–C5–C10, 7.5(2)° for C5–S1–C4–Cl4, 82.1(4)° for C4–C3–C2–C1 and 4.1(3)° for O2–N1–C3–C2, respectively.

5. Conclusions

In summary, novel *S*-, *S*,*S*-, *S*,*S*,*S*-, *S*,*O*- and *N*,*S*-substituted compounds have been synthesized under different reaction conditions and their structures were characterized by spectroscopic methods. In addition, the crystal structure of **4a** was firmly secured by X-ray crystallography.

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Povzetek

Z reakcijo nekaterih tiolov in 2-nitropentakloro-1,3-butadiena smo pripravili različne tiosubstituirane nitrodienske spojine (**3**, **4a**, **5a**,**b**, **6c**, **7a**, **7c**, **9**). *N*,*S*-Substituirane nitrodiene (**11a**–**g**, **13**, **15**) smo pripravili iz 2-nitropentakloro-1,3-butadiena z izbranimi amini (morfolin in derivati piperazina). Spojina **4a** je kristalizirala v triklinski singoniji (prostorska skupina P-1) s parametri osnovne celice: a = 6.6525(7) Å, b = 10.7906(5) Å, c = 10.8339(4) Å, α = 72.57(3)°, β = 84.23(4)°, γ = 75.81(3)°, V = 719.03(9) Å^3, Z = 2. Nove spojine smo karakterizirali z elementno analizo, UV-VIS, FT-IR, ^{1}H-NMR, NMR (^{13}C ali APT) in masno spektroskopijo.