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, thio substituted nitro diene compounds (3, 4a, 5a,b, 6c, 7a, 7c, 9) were obtained from the reactions of some thiols with 2-nitropentachloro-1,3-buta diene. N,S-Substituted nitro diene compounds (11a-g, 13, 15) were obtained from 2-nitropentachloro-1,3-buta diene 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) Å3, Z = 2. The novel compounds were characterized by elemental analysis, UV-VIS, FT-IR, 1H-NMR, NMR (13C or APT) and mass spectroscopy.

Keywords: 1,3-Butadiene, thiocethers, N,S-substituted nitro dienes, crystal structure.

1. Introduction

Due to the SN reactivity patterns, nitro substituted polyhalogeno-1,3-buta dienes have proven to be valuable synthetic precursors for the formation of a variety of polyfunctionalized bioactive heterocycles.1-2 The thio substituted 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,O-, S,S,S-, S,S,S-, S,O-, N,S-substituted nitro dienes 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 nitro dienes 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 thio substituted 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. 1H and 13C 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 60F254 (Merck, Darmstadt), detection with ultraviolet light (254 nm).

2.2. Synthesis

S,O-Substituted nitro diene compound 3 was obtained from the reactions of 2-nitropentachloro-1,3-buta diene with 2-mercaptophenol. The reaction of 2-nitropentachloro-1,3-bu-

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

Butadiene 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

Ibis and Ozkok: *The Synthesis of Novel S-, S,S-, S,S,S-, S,O-, N,S-Substituted Halogenobuta-1,3-dienes*
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 shown 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 nitrode 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-1,3,4,4-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 Na2SO4. After filtering, the solvent was evaporated and the residue was purified by column chromatography on silicagel. (Scheme 1)

2. 3. 2. General Procedure for 2

Equimolar amounts of 2-nitro-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 Na2SO4. After filtering, the solvent was evaporated and the residue was purified by column chromatography 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 CH2Cl2 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 Na2SO4. After filtering, the solvent was evaporated and the residue was purified by column chromatography 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-1,3,4,4-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%). Rf (petroleum ether): 0.35. IR (KBr, cm-1): ν 3096 (C–H arom), 1600, 1618 (C=C), 1294, 1547 (C–NO2). UV-VIS (CHCl3): λmax (log ε) 240.88 (4.76), 374.52 (4.77) nm; 1H NMR (499.74 MHz, CDCl3, 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). MS [ESI+]: m/z 326 [M+H]+. Anal. Calcd for C13H8Cl2NO3S (M = 324.57 g/mol): 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%). Rf [petroleum ether/CHCl3 (1:1)]: 0.46. IR (KBr, cm-1): ν 3056 (C–H arom), 2921, 2986 (C–H), 1599 (C=O), 1533 (C–NO2). UV-VIS (CHCl3): λmax (log ε) 240.88 (4.1), 344.27 (4.2) nm; 1H NMR (499.74 MHz, CDCl3, ppm): δ 2.43 (t, 3H, CH3), 7.29–7.36 (m, 8H, H arom), 7.44–7.52 (m, 2H, H arom). APT NMR (125.66 MHz, CDCl3, ppm): δ 19.5 (CH3), 120.35, 127.36, 127.37, 127.76, 142.35, 156.81 (Cbutad, C arom), 126.26, 12.30, 131.04, 135.87 (CH arom). MS [APCI+]: m/z 277 [M–Cl–NO2]+, 278 [M+H]+. Anal. Calcd for C14H13Cl2NO3S (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-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%). Rf [petroleum ether/CHCl3 (1:1)]: 0.51. IR (KBr, cm-1): ν 3061 (C–H arom), 2854, 2925 (C–H), 1296, 1518 (C–NO2). UV-VIS (CHCl3): λmax (log ε) 239.35 (4.1), 259.92 (4.1), 366.70 (3.8) nm; 1H NMR (499.74 MHz, CDCl3, ppm): δ 2.48 (s, 6H, CH3), 6.97–7.56 (m, 8H, H arom). 13C NMR (125.66 MHz, CDCl3, 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 C14H13Cl2NO3S (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-pentachloro-1,3-butadiene (1) (2.00 g, 7.37 mmol) with 2-carboxyphenylthiol (0.91 g, 7.36 mmol) according to the general procedure 1.

Ibis and Ozok: *The Synthesis of Novel S-, S,S-, S,S,S-, S,O-, N,S-Substituted Halogenobuta-1,3-dienes*
tachloro-1,3-butadiene (I) (2.00 g, 7.37 mmol) with 2-mercaptopalicylic acid (1.13 g, 7.36 mmol) according to the general procedure 1.

5b: Yellow solid, mp: 206–207 °C. Yield: 1.89 g (51%). Rf (CHCl₃): 0.50. IR (KBr, cm⁻¹): ν 2871, 2975, 3064 (C=H_arom), 3384 (COOH), 1618 (C=O), 1269, 1416 (C–NO₂). UV-VIS (CHCl₃): λ_max (log ε) 239.16 (3), 262.64 (2.8) nm; 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). MS [ESI⁺]: m/z 507 [M+H]⁺. Anal. Calcd for C₁₈H₁₂Cl₂NO₃S₂ (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%). Rf [petroleum ether/CHCl₃ (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–NO₂). UV-VIS (CHCl₃): λ calculated (log ε) 244.58 (2.8), 272.75 (2.6), 372.9 (2.8) nm; δ 1.81 (s, 3H, CH₃), 2.10 (s, 3H, CH₃), 2.21 (s, 6H, CH₂), 2.23 (s, 6H, CH₂), 6.72–6.92 (m, 9H, H_arom). MS [ESI⁺]: m/z 576 [M–H]⁻. Anal. Calcd for C₂₅H₂₁Cl₂N₂O₂S₃ (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 1,1,4-Tris(2,4-dimethylphenylthio)-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%). Rf (CHCl₃): 0.51. IR (KBr, cm⁻¹): ν 3049, 2974, 2937 (C–H_arom), 2738, 2676, 2491 (C–H), 1593 (C=C), 1286, 1537 (C–NO₂). UV-VIS (CHCl₃): λ_max (log ε) 241.18 (3.1), 260.76 (3), 362.43 (2.9) nm; δ 1.79 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 6.82–7.20 (m, 10H, H_arom). MS [ESI⁻]: m/z 533 [M–H]⁻. Anal. Calcd for C₂₅H₂₁Cl₂NO₂S₃ (M = 534.54 g/mol): C, 56.17; H, 3.96; N, 2.62; S, 18.00. 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%). Rf [petroleum ether/CHCl₃ (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–NO₂). UV-VIS (CHCl₃): λ_max (log ε) 244.58 (2.8), 272.75 (2.6), 372.9 (2.8) nm; δ 1.81 (s, 3H, CH₃), 2.10 (s, 3H, CH₃), 2.21 (s, 6H, CH₂), 2.23 (s, 6H, CH₂), 6.72–6.92 (m, 9H, H_arom). MS [ESI⁺]: m/z 576 [M+H]⁺. Anal. Calcd for C₂₅H₂₁Cl₂N₂O₂S₃ (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 (I) (2.00 g, 7.37 mmol) with 4,4’-thiobisbenzenethiol (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%). Rf [petroleum ether/CHCl₃ (1:1)]: 0.47. IR (KBr, cm⁻¹): ν 3050, 3069 (C–H_arom), 1639 (C=C), 1472, 1565 (C–NO₂). UV-VIS (CHCl₃): λ_max (log ε) 255 (4.3) nm; δ 7.04–7.06 (m, 4H, H_arom); 7.17–7.19 (m, 4H, H_arom). MS [ESI⁺]: m/z 721 [M+H]⁺. Anal. Calcd for C₃₃H₁₉Cl₂N₂O₂S₁₂ (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)-2-fluorophenyl]piperazin-4-one (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-fluorophenyl)piperazinone (0.25 g, 1.38 mmol) according to the general procedure 3.

11a: Yellow crystals, mp: 181–182 °C. Yield: 0.39 g (55%). Rf (CHCl₃): 0.37. IR (KBr, cm⁻¹): ν 3066 (C–H_arom), 2827, 2922 (C–H), 1595, 1610 (C=C), 1271, 1542 (C–NO₂). UV-VIS (CHCl₃): λ_max (log ε) 242.24 (2.9), 282.37 (2.5), 389.39 (2.8) nm; δ 1H NMR (499.74 MHz, CDCl₃, ppm): δ 2.37 (s, H, CH₃), 2.85 (brs, 4H, N, S-Substituted Halogenobuta-1,3-dienes
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%). Rf/EtAc: 0.39. IR (KBr, cm−1): ν 3066 (C–Harom.), 2827, 2922 (C–H), 1595, 1610 (C=C), 1271, 1542 (C–NO2). UV-VIS (CHCl3): λmax (log ε) 245.89 (3.4), 293.05 (2.7), 298.65 (3.2) nm; 1H NMR (499.74 MHz, CDCl3, ppm): δ 19.73 (CH3), 48.56, 51.98 (C piper), 118.77, 124.2, 125.67, 139.04, 145.66, 155.89, 158.80, 166.67 (CButad 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 C21H19Cl3FN3O2S (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-(1-phenylmethyl)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-(1-phenylmethyl)piperazine (0.25 g, 1.38 mmol) according to the general procedure 3.

11e: Yellow crystals, mp: 181–182 °C. Yield: 0.44 g (55%). Rf (CHCl3): 0.38. IR (KBr, cm−1): ν 3019, 3059 (C–Harom.), 2821, 2911, 2972 (C–H), 1586 (C=C), 1282, 1530 (C–NO2). UV-VIS (CHCl3): λmax (log ε) 245.5 (2.4), 3436 (2.3), 398.19 (3.6) nm; 1H NMR (499.74 MHz, CDCl3, ppm): δ 2.29 (s, 3H, CH3), 3.36 (brs, 4H, H piper), 4.09 (s, H, CH), 7.08–7.27 (m, 14H, H arom). 13C NMR (125.66 MHz, CDCl3, ppm): δ 19.66, 49.84 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 C25H26Cl3N4O3S (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-flourophenyl)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-flourophenyl)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%). Rf [CHCl3/EtAc (1:1)]: 0.45. IR (KBr, cm−1): ν 3436 (C–Harom.), 2870 (C–H), 1598 (Ar–NO2), 1285, 1513 (C–NO2). UV-VIS (CHCl3): λmax (log ε) 245.5 (2.4), 377.08 (3.1) nm; 1H NMR (499.74 MHz, CDCl3, ppm): δ 2.49 (s, 3H, CH3), 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, CDCl3, ppm): δ 20.97 (CH3), 46.31, 52.10
(C$_{15}$H$_{18}$Cl$_3$N$_3$O$_3$S $\mu$Na$^+$. Anal. Calcd for C$_{15}$H$_{18}$Cl$_3$N$_3$O$_3$S $\mu$Na$^+$: m/z 553 [M+Na]$^+$. Anal. Calcd for C$_{21}$H$_{20}$Cl$_3$N$_3$O$_3$S ($M = 438.87$ 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 $\lambda = 0.71073$ Å. The data were collected at a temperature of 20 °C to a maximum 2θ 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 ellipsoids 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 cyclic 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...
The protonated molecular ion peak of 6c was observed at m/z 476 in the mass spectrum. In the 1H-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 1H-NMR spectrum of compound 9 of the aromatic protons two doublets located at δ 7.04–7.06 and 7.17–7.19 ppm were observed. In the 13C-NMR of the compound 11d methoxy group appeared at δ 55.72 ppm. The same methoxy group in the 1H-NMR spectrum of 11d was observed at δ 3.82 ppm as a singlet. In the 1H-NMR spectrum of the compound 11e CH group proton appeared at δ 4.09 ppm as a singlet; accordingly in the 13C-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 1H-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, 1H-NMR, 13C or APT NMR, MS and UV/VIS).

In our previous study the monothiosubstituted nitrodiene compound 1,3,4,4-tetrachloro-4-(4-chlorophenylsulfonyl)-2-nitrobuta-1,3-diene crystallized in the triclinic crystal system. 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) Å³, Z = 2.

The torsion angles and geometric structure of compounds 1,3,4,4-tetrachloro-4-(4-chlorophenylsulfonyl)-2-nitrobuta-1,3-diene 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 length C1–C2 is 1.305(4) Å, C2–C3 1.467(3) Å and C3–C4 1.356(3) Å.

Table 1. Crystallographic data and structure refinement for 4a

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{11}H_{7}Cl_{4}NO_{2}S</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>359.05</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P-1</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>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)°</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>719.03(9)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>D_{calc} (g/cm³)</td>
<td>1.658</td>
</tr>
<tr>
<td>μ [mm⁻¹]</td>
<td>0.961</td>
</tr>
<tr>
<td>F_{000}</td>
<td>360.00</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>39062</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2547 (R_{int} = 0.029)</td>
</tr>
<tr>
<td>Goodness-of-fit on F</td>
<td>1.014</td>
</tr>
<tr>
<td>Final R indices [I &gt; 3σ(I)]</td>
<td>R = 0.039, wR = 0.053</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.57 and –0.31 e.Å⁻³</td>
</tr>
</tbody>
</table>

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

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

Figure 1. The molecular structure of compound 4a (ORTEP III). Displacement ellipsoids are shown at the 50% probability level.
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–C14, 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.

6. Acknowledgements

We thank the Research Fund of the University of Istanbul for financial support of this work.

7. References

17. Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC- 821368 for 4a. E-mail: deposit@ccdc.cam.ac.uk.

Povzetek

Z reakci je nekaterih tiolov in 2-nitropentaklooro-1,3-butađiana 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-nitropentaklooro-1,3-butađiana z izbranimi aminami (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) Å³, Z = 2. Novo spojino smo karakterizirali z elementno analizo, UV-VIS, FT-IR, 1H-NMR, NMR (13C ali APT) in masno spektroskopijo.