Synthesis and spectral properties of new piperazine derivatives and a structural study

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In this study, new piperazine derivatives were synthesized by the reactions of S-substituted-3-nitro-1,3-butadienes with some piperazine derivatives: (1-(2-furoyl)-, 1- (4-fluorobenzyl)-, 1- (3-fluorophenyl)- and 1- (1-tetrahydro-2-furyl)piperazine) in CHCl₃ at room temperature. The structures of the new compounds were characterized by micro analysis, FT-IR, MS spectrometry, ¹H- and ¹³C-NMR. The crystal structure analysis was performed on the synthesized compound 5d by using the X-ray diffraction method. The compound 5d crystallizes in the monoclinic space group P2₁/c with a = 12.5503(2) Å, b = 11.2039(2) Å, c = 14.1007(4) Å, Z = 4. The structure was solved by direct methods (SIR92) and refined to the residual index R₁ = 0.031.

Keywords: Piperazine derivatives; X-ray study; Organic synthesis; Vinylic substitution

INTRODUCTION

Polyhalo-substituted-1,3-butadienes possess a broad spectrum of useful properties: they are employed as monomers for the preparation of valuable polymers and copolymers resistant to heat, light and chemical corrosion, and exhibit algicidal, bactericidal and fungicidal activities [1]. Moreover, the precursor perchloronitrobutadiene 1 proved to be active against cancer cells [2].

Piperazine analogues have drawn great interest for their biological activities in a number of different therapeutic areas [3]. These include anticancer, antifungal [4,5], antibacterial, antimalarial and antipsychotic agents [6], as well as HIV protease inhibitors and antidepressants. Also, the N-carbonyl piperazine moieties exhibit cardiovascular properties [7].

EXPERIMENTAL

General

Melting points were measured on a Büchi B-540 melting point apparatus. FTIR spectra (cm⁻¹) were recorded as KBr pellets in nujol mulls on a Shimadzu IR Prestige 21 model Diamond spectrometer (ATR method). ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova spectrometer at 499.83 MHz for ¹H and 125.48 MHz for ¹³C using CDCl₃ as a solvent and TMS as an internal standard. Mass spectra were obtained on a hybrid triple quadrupole linear ion trap mass spectrometer (4000 QTRAP, ABSciex). The 4000 QTRAP was operated in the triple quadruple mass spectrometer mode by use of electrospray ionization (ESI) source. The crystal structure of compound 5d was determined on Rikagu R-Axis Rapid-S X-Ray Single Crystal diffractometer. Micro analyses (C, H, N, S) were conducted using the Thermo Finnigan Flash EA 1112 elemental analyzer. Products were isolated by column chromatography on silica gel (Fluka Silica gel 60, particle size 63–200 μm). Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC). All chemicals were of reagent grade and were used without further purification. Moisture was excluded from the glass apparatus with CaCl₂ drying tubes.

General Method 1 for the synthesis of S-substituted-3-nitrobutadiene Compounds (3a-d)

4-(Hexadecylsulfanyl)-1,1,2,4-tetrachloro-3-nitro-1,3-butadiene (3a) [8], 4-(cyclopentylsulfanyl)-1,1,2,4-tetrachloro-3-nitro-1,3-butadiene (3b) [9], 4-(octadecyl-sulfanyl)-1,1,2,4-tetrachloro-3-nitro-1,3-butadiene (3c) [8] and 4-(ethylsulfanyl)-1,1,2,4-tetrachloro-3-nitro-1,3-butadiene (3d) [10] were synthesized by the reactions of 1 with 2a-d according to the literature [8-10].

General method 2 for the synthesis of piperazine derivatives

The S-substituted-3-nitro-1,3-butadienes 3a-d and equimolar amounts of the piperazine derivatives were stirred in chloroform (25 mL) for 8 h. Chloroform (30 mL) was added to the reaction mixture. The organic layer was washed with water (4+30 mL), and dried with Na₂SO₄. After the solvent was evaporated the residue was purified by column chromatography on silica gel.

{4-(1-(2-Furoyl)piperazin-1-yl)-4-(4-hexadecylsulfanyl)-1,1,2-trichloro-3-nitro-1,3-butadiene (5a): Compound 5a was synthesized by the reaction

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of 3a (0.1 g, 0.2 mmol) with 1-(2-furoyl)piperazine 4 (0.036 g, 0.2 mmol) according to general method 2. Yellow oil, yield: 0.062 g, 49%. Rf: 0.64 [PET:EtAc (2:1)]. FT-IR (KBr, cm⁻¹): ν = 2952, 2853 (C-H), 1649 (C=Oamide), 1570 (C-C), 1529, 1487, 1274 (NO₂). 1H NMR (CDCl₃, ppm): δ = 0.86-0.92 (t, 3H, CH₃), 1.24-1.32 (m, 2H, CH₂), 1.37-1.43 (m, 2H, CH₂), 1.65-1.72 (m, 2H, CH₂), 2.97-3.10 (s, 2H, S-CH₂), 3.40-3.85 (sbr, 4H, CH₂piper), 4.05-4.32 (s, 4H, CH₂piper), 6.53-6.57 (m, 1H, Hasonom), 7.15-7.17 (d, 1H, Hasonom), 7.52-7.55 (s, 1H, Hasonom). 13C NMR (CDCl₃, ppm): δ = 14.14 (CH₃), 23.71, 28.73, 29.04, 29.37, 29.39, 29.53, 29.62, 29.67, 29.70, 31.75 (CH₃), 31.94 (S-CH₂), 35.66, 52.91 (Cpiper), 111.79, 118.00, 118.83 , 125.04, 126.53, 144.31 (Cbutad, Asonom), 147.28 (Cfuryl), 169.30 (C=O). MS [+ESI]: m/z (%) 638 (100) [M+H]+. Micro analysis: C₂₃H₂₅Cl₃N₃O₂S, (Mₐ = 637.1 g/mol). Calculated: C, 54.69; H, 6.96; N, 6.60; S, 5.03%; Found: C, 54.69; H, 7.00; N, 6.62; S, 5.02%.

\[
\text{[4-(1-(2-Furoyl)piperazin-1-yl)-4-(4-octadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butenadiene (5c): Compound 5c was synthesized by the reaction of 3c (0.1g, 0.2 mmol) with 1-(2-furoyl)piperazine 4 (0.035 g, 0.2 mmol) according to general method 2. Yellow oil, yield: 0.053 g, 42%. Rf: 0.30 [PET:EtAc (2:1)]. FT-IR (KBr, cm⁻¹): ν = 2952, 2853 (C-H), 1649 (C=OAmide), 1570 (C-C), 1529, 1487, 1274 (NO₂). 1H NMR (CDCl₃, ppm): δ = 0.87-0.90 (t, 3H, CH₃), 1.25-1.32 (m, 28H, CH₂), 1.39-1.42 (m, 2H, CH₂), 1.67-1.70 (m, 2H,CH₂), 2.97-3.00 (d, 2H, S-CH₂), 3.99 (sbr, 8H, CH₂piper), 6.53-6.54 (s, 1H, Hasonom), 7.13-7.14 (s, 1H, Hasonom), 7.51-7.52 (s, 1H, Hasonom). 13C NMR (CDCl₃, ppm): δ = 14.12 (CH₃), 22.69, 28.72, 29.02, 29.36, 29.38, 29.52, 29.61, 29.66, 29.70, 29.74 (CH₃), 31.92 (S-CH₂), 35.63, 52.89 (Cpiper), 111.75, 117.94, 118.86 , 125.00, 126.54, 144.28, 158.99 (Cbutad, Asonom), 147.27 (Cfuryl), 169.63 (C=O). MS [+ESI]: m/z (%) 688 (100) [M+Na]+. Micro analysis: C₃₁H₃₆Cl₃N₃O₂S, (Mₐ = 665.15 g/mol). Calculated: C, 55.98; H, 7.27; N, 6.32; S, 4.82%; Found: C, 55.99; H, 7.29; N, 6.35; S, 4.86%.

\[
\text{[4-(1-(2-Furoyl)piperazin-1-yl)-4-(ethyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butenadiene (5d): Compound 5d was synthesized by the reaction of 3d (0.1g, 0.34 mmol) with 1-(2-furoyl)piperazine 4 (0.057 g, 0.32 mmol) according to general method 2. Yellow oil, yield: 0.057 g, 46%. M.p.: 135.8-136.0°C.}
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\text{[4-(1-(4-Fluorobenzyl)piperazin-1-yl)-4-(4-hexadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butenadiene (7a): Compound 7a was synthesized by}
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[4-(1-(4-Fluorobenzyl)piperazin-1-yl)-4-(4-octadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butenadiene (7b): Compound 7b was synthesized by the reaction of 3b (0.1g, 0.3 mmol) with 1-(4-fluorobenzyl)piperazine 6 (0.058 g, 0.3 mmol) according to general method 2. Orange solid, yield: 0.074 g, 51%. Rf : 0.41 [PET:EtAc (2:1)]. FT-IR (KBr, cm⁻¹): ν = 3052, 2961, 2871, 2805, 2768 (C-H), 1602 (C=C), 1529, 1278 (NO₂). 1H NMR (CDCl₃, ppm): δ = 1.52-1.76 (m, 4H, CH₂cyclo), 1.65-1.73 (s, 4H, CH₂cyclo), 2.55 (sbr, 3H, S-CH₂cyclo, and Ph-CH₂), 3.45 (s, 4H, CH₂piper), 3.50-3.91 (sbr, 4H, CH₂piper), 6.90-7.00 (t, 2H, CH₃arom), 7.19-7.21 (m, 2H, CH₃arom). 13C NMR (CDCl₃, ppm): δ = 24.61, 48.26 (Ccyclo), 52.52, 53.35 (Cpiper), 115.26, 115.43, 118.12, 124.6, 126.88, 130.7, 130.53, 132.82, 161.26 (Cbutad, Asonom), 163.21 (Cfuryl). MS [+ESI]: m/z (%) 494 (100) [M+H]+. Micro analysis: C₃₀H₂₃Cl₂FN₃O₃S, (Mₐ = 494.84 g/mol). Calculated: C, 48.54; H, 4.68; N, 8.49; S, 6.48%; Found: C, 48.59; H, 4.69; N, 8.51; S, 6.47%.

[4-(1-(4-Fluorobenzyl)piperazin-1-yl)-4-(4-octadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butenadiene (7c): Compound 7c was synthesized by the reaction of 3c (0.1g, 0.19 mmol) with 1-(4-fluorobenzyl)piperazine 6 (0.037 g, 0.19 mmol) according to general method 2. Oil, yield: 0.055 g, 43%. Rf: 0.59 [PET:EtAc (2:1)]. FT-IR (KBr, cm⁻¹): ν = 2924, 2853 (C-H), 1610 (C=C), 1529, 1278 (NO₂) 1H NMR (CDCl₃, ppm): δ = 0.78-0.82 (t, 3H, CH₃), 1.15-1.25 (m, 28H, CH₂), 1.28-1.35 (m, 2H, CH₂), 1.50-1.60 (m, 2H, CH₂), 2.55-2.75 (sbr, 2H, Ph-CH₂), 2.85-2.93 (t, 2H, S-CH₂), 3.45-3.58 (s, 4H, CH₂piper), 3.62-3.83 (sbr, 4H, CH₂piper), 6.96-6.99 (t, 2H, CH₃arom), 7.23-7.29 (sbr, 2H,
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CH$_{atom}$. $^{13}$C NMR (CDCl$_3$, ppm): δ=64.15 (CH$_3$), 22.71, 28.69, 29.0, 29.38, 29.52, 29.62, 29.68, 29.71, 29.76, 31.94 (CH$_3$), 35.51 (S-CH$_2$), 61.48 (Ph-CH$_2$), 115.58, 128.02, 130.50, (C$_{butad}$, C$_{arom}$). MS [+ESI]: m/z (%) 680 (100) [M+H]$.^+$ Micro analysis: C$_{39}$H$_{36}$Cl$_3$F$_4$N$_6$O$_6$S$_3$ (M$_a$ = 679.2 g/mol). Calculated: C, 58.38; H, 7.57; N, 6.19; S, 4.72%; Found: C, 58.38; H, 7.58; N, 6.20; S, 4.75%.

$\text{[4-[(3-Fluorophenyl)piperazin-1-yl]-4-(4-hexadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butadiene (9a):}$ Compound 9a was synthesized by the reaction of 3a (0.1g, 0.2 mmol) with 1-(3-fluorophenyl)piperazine 8 (0.037 g, 0.2 mmol) according to general method 2. Orange solid, yield: 0.049 g, 35%. R$_r$: 0.33 [PET:EtAc (4:1)]. M.p.: 97°C.

$\text{[4-[(3-Fluorophenyl)piperazin-1-yl]-4-(4-octadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butadiene (9c):}$ Compound 9c was synthesized by the reaction of 3c (0.1g, 0.19 mmol) with 1-(3-fluorophenyl)piperazine 8 (0.034 g, 0.3 mmol) according to general method 2. Orange solid, yield: 31%. R$_r$: 0.52 [PET:EtAc (4:1)]. M.p.: 96-97°C.

FT-IR (KBr, cm$^{-1}$): ν= 2926, 2854 (C-H), 1615 (C=C), 1528, 1265 (NO$_2$). $^1$H NMR (CDCl$_3$, ppm): δ= 0.77-0.84 (t, 3H, CH$_3$), 1.18-1.24 (d, 3OH, CH$_2$), 1.50 (s, 2H, CH$_2$), 2.90 (s, 2H, S-CH$_2$), 3.30 (s, 4H, C$_{pip}$), 3.65-4.10 (sbr, 4H, C$_{pip}$), 6.50-6.64 (m, 2H, H$_{arom}$), 7.14-7.20 (m, 2H, H$_{arom}$). $^{13}$C NMR (CDCl$_3$, ppm): δ= 29.39, 29.70, 29.71, 29.82, 29.83, 30.01, 30.81, 31.94, 32.90, 33.04, 33.07, 34.51, 35.61, 50.73, 63.72 (g/mol). Calculated: C, 57.80; H, 7.44; N, 6.32; S, 4.82%; Found: C, 57.80; H, 7.44; N, 6.35; S, 4.83%.

$\text{[4-[(Tetrahydro-2-furyl)piperazin-1-yl]-4-(4-hexadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butadiene (11a):}$ Compound 11a was synthesized from the reaction of 3a (0.1g, 0.19 mmol) with 1-(1-tetrahydro-2-furyl)piperazine 10 (0.037 g, 0.19 mmol) according to general method 2. Yellow oil, yield: 0.043 g, 34%. R$_r$: 0.67 [PET:EtAc (1:1)]. FT-IR (KBr, cm$^{-1}$): ν= 2952, 2853 (C-H), 1659 (C=O), 1529, 1273 (NO$_2$). H NMR (CDCl$_3$, ppm): δ= 0.88-1.03 (t, 3H, CH$_3$), 1.21-1.26 (m, 28H, CH$_2$), 1.30-1.48 (m, 2H, CH$_2$), 1.58-1.65 (m, 2H, CH$_{3fury}$), 2.95-2.98 (s, 2H, S-CH$_2$), 3.60-3.82 (m, 2H, CH$_{2fury}$), 3.84-3.97 (m, 8H, C$_{pip}$), 4.57-4.59 (t, 1H, CH$_{fury}$). $^{13}$C NMR (CDCl$_3$, ppm): δ= 14.12 (CH$_3$), 22.69, 25.58, 25.79, 27.90, 28.70, 29.02, 29.35, 29.51, 29.60, 29.65, 29.67, 29.71, 29.70, 29.75, 31.92 (CH$_3$), 35.61 (S-CH$_3$), 41.75, 44.73 47.51 (C$_{fury}$), 51.77, 53.49 (C$_{pip}$), 69.18 (C$_{fury}$), 118.77, 124.97, 126.56 (C$_{butadien}$), 169.88 (C=O). MS [+ESI]: m/z (%) 664 (100) [M+Na]$^+$. Micro analysis: C$_{41}$H$_{33}$Cl$_3$F$_4$N$_6$O$_6$S$_3$ (M$_a$ = 641.13 g/mol). Calculated: C, 54.33; H, 7.55; N, 6.55; S, 5.00%; Found: C, 54.37; H, 7.56; N, 6.58; S, 5.02%.

$\text{[4-[(Tetrahydro-2-furyl)piperazin-1-yl]-4-(4-octadecyl-sulfanyl)-1,1,2-trichloro-3-nitro-1,3-butadiene (11c):}$ Compound 11c was synthesized from the reaction of 3c (0.1g, 0.19 mmol) with 1-(1-tetrahydro-2-furyl)piperazine 10 (0.353 g, 0.19 mmol) according to general method 2. Yellow solid, yield: 0.065 g, 51%. R$_r$: 0.42 [PET:EtAc (1:1)]. M.p.: 120°C. FT-IR (KBr, cm$^{-1}$): ν= 2952, 2853 (C-H), 1659 (C=O), 1613 (C=C), 1529, 1273 (NO$_2$). $^1$H NMR (CDCl$_3$, ppm): δ= 0.79-0.83 (t, 3H,
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CH\textsubscript{3}), 1.15-1.25 (m, 28H, CH\textsubscript{3}), 1.28-1.35 (m, 4H, CH\textsubscript{2} \textsubscript{furyl}), 1.47-1.53 (s, 2H, CH\textsubscript{2} \textsubscript{furyl}), 2.87-2.97 (s, 2H, S-CH\textsubscript{2} \textsubscript{furyl}), 3.20-3.30 (s, 4H, C\textsubscript{2} \textsubscript{CH\textsubscript{2}furyl}), 3.50-4.00 (sbr, 4H, C\textsubscript{2} \textsubscript{CH\textsubscript{2}furyl}), 6.65-6.70 (d, 1H, H\textsubscript{arom}), 6.90 (d, 1H, H\textsubscript{arom}), 7.25-7.30 (d, 1H, H\textsubscript{arom}), 13\textsuperscript{C} NMR (CDCl\textsubscript{3}, ppm): \(\delta=14.15\) (CH\textsubscript{3}), 22.71, 28.71, 29.04, 29.36, 29.53, 29.63, 29.68, 29.71, 29.80, 31.94, 35.63 (CH\textsubscript{3}), 48.79 (C\textsubscript{piper}), 103.29, 103.48, 107.47, 111.65, 130.53 (C\textsubscript{butad}, C\textsubscript{arom}). MS [+ESI]: m/z (%) 738 (100) [M+Na]\textsuperscript{+}. Micro analysis: C\textsubscript{12}H\textsubscript{14}Cl\textsubscript{3}N\textsubscript{2}O\textsubscript{2}S, (M\textsubscript{a} = 716.07 g/mol) . Calculated: C, 53.67; H, 6.76; N, 5.87; S, 4.48%; Found: C, 53.72; H, 6.79; N, 5.88; S, 5.89%.

**X-Ray Crystallography**

Yellow crystals of compound \textbf{5d} suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol/chloroform (10:1) solution at room temperature. The compound \textbf{5d}, C\textsubscript{12}H\textsubscript{14}Cl\textsubscript{3}N\textsubscript{2}O\textsubscript{2}S, having approximate dimensions of 0.60 \times 0.30 \times 0.20 mm, was mounted on a glass fiber. All measurements were made on a Rigaku R-Axis Rapid-S imaging plate area detector with graphite monochromated Mo-K\textsubscript{a} radiation (\(\lambda = 0.71073\) Å). The crystal structures were solved by SIR 92 [12] and refined with CRYSTALS [13]. 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\textsubscript{iso}(H) = 1.2U\textsubscript{eq}(C). Drawing was performed with the program ORTEP-III [14] with 50% probability displacement ellipsoid. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers. CCDC-1544558 for compound \textbf{5d} [15].

**RESULTS AND DISCUSSION**

The aim of this study was to synthesize new piperazine derivatives \textbf{5a, 5c-d, 7a-c, 9a-c, 11a, 11c and 13b-c} and to determine the exact structures of the new compounds by using spectroscopic techniques (\textsuperscript{1}H NMR, \textsuperscript{13}C NMR, FTIR, MS) and X-ray diffraction method. In this work, the S-substituted-3-nitro-1,3-butadienes were obtained by direct reactions of pentachloro-3-nitrobutadiene with some S-nucleophiles [hexacyclilthio-, cyclopentylthiol, octadecylthiol and ethylthiol] [8-10].

The novel piperazine derivatives \textbf{5a, 5c, 5d} [11], \textbf{7a-c, 9a-c, 11a, 11c and 13b-c} were synthesized by the reaction of the S-substituted-3-nitro-1,3-butadienes ( \textbf{3a} [8], \textbf{3b} [9], \textbf{3c} [8] and \textbf{3d} [10]) with (1-(2-furoyl)piperazine, 1-(4-fluorobenzyl) piperazine, 1-(3,4-dichlorophenyl) piperazine 2 in CHCl\textsubscript{3}, respectively, as shown in Scheme 1.
The FT-IR spectra of compounds 5a and 5c, 11a and 11c showed the absorption bonds of the amide carbonyl group at 1649 and 1659 cm\(^{-1}\), respectively. The proton NMR data of compounds 5a, 5c, 7a-c, 9a-c and 13b-c showed the aromatic protons within the range 6.42-7.55 ppm. In the \(^{13}\)C NMR spectra of all compounds signals were observed at 49-62 ppm for the methylene carbon atom of the piperazine ring. Due to the aromatic ring of furoyl, in the carbon NMR spectra of compounds 5a and 5c signals were observed at \(\delta = 147\) ppm for the furoyl (C-O) carbons. The (C-O) signals of the tetrahydrofuroyl units were observed at 69 ppm in the carbon NMR spectra of 11a and 11c. The carbon NMR shift of the carbonyl groups of compounds 5a, 5c, 11a and 11c appeared around \(\delta = 169-170\) ppm. The (+ESI) mode mass spectra of 5c revealed at \(m/z\) (%) 688 (100) [M+23]\(^+\) which corresponds to the addition of one sodium ion. The (+ESI) mass spectrum of 5c is shown in Fig. 1.

**Scheme 1.** Synthesis of piperazine derivatives.

**X-ray study**

The crystals used in the X-ray diffraction study were obtained by recrystallization of compound 5d from a solution of ethanol-chloroform (10:1). The crystal structure of compound 5d is shown in Fig. 2.
The butadiene unit is not planar as would be if the two double bonds were fully conjugated. Non-coplanar structures of the butadiene fragments of these molecules and the clear C2-C3 single bonds 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 non-planar molecular structure relative to 1,4-addition. Crystal data and refinement parameters are summarized in Table 1 and the selected bond distances, bond and torsion angles are listed in Table 2 for compound 5d.

The nitro group is nearly coplanar with the butadiene unit to which it is attached, with torsion angles of (O1–N1–C3–C2) and (O1–N1–C3–C4) -11.3(4)° and 167.0(3)°, respectively. The four carbon atoms of the piperazine ring (C7-C8-C9-C10) are planar with a maximum deviation of 0.0102(1)Å and they adopt a chair conformation; the perpendicular distances of the two chair atoms

### Table 1. Main crystallographic parameters of compound 5d

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<td>Cell formula units (Z)</td>
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<td>Final R indices [I/2σ(I)]</td>
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### Table 2. Selected bond distances (Å), bond and torsion angles (°) for compound 5d

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<th>Bond angles</th>
<th>Torsion angles</th>
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<td>C1-C2</td>
<td>1.330(4)</td>
<td>C1-C2-C3 124.4(3) C1-C2-C3-C4 -60.2(5)</td>
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<td>C2-C3</td>
<td>1.459(4)</td>
<td>C2-C3-C4 124.0(3) N2-C8-C9-N3 52.4(3)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.398(4)</td>
<td>O1-N1-O2 122.3(3) N2-C7-C10-N3 -56.4(3)</td>
</tr>
<tr>
<td>C4-S1</td>
<td>1.734(3)</td>
<td>C7-N2-C8 112.1(2) C2-C3-C4-S1 -38.2(3)</td>
</tr>
<tr>
<td>C4-N2</td>
<td>1.338(4)</td>
<td>C9-N3-C10 112.5(3) C2-C3-C4-N2 140.2(3)</td>
</tr>
<tr>
<td>C11-O3</td>
<td>1.204(4)</td>
<td>C11-C11-C12 113.5(2) C1-C2-C3-N1 118.1(4)</td>
</tr>
</tbody>
</table>

The nitro group is nearly coplanar with the butadiene unit to which it is attached, with torsion angles of (O1–N1–C3–C2) and (O1–N1–C3–C4) -11.3(4)° and 167.0(3)°, respectively. The four carbon atoms of the piperazine ring (C7-C8-C9-C10) are planar with a maximum deviation of 0.0102(1)Å and they adopt a chair conformation; the perpendicular distances of the two chair atoms.
in the para positions (N2 and N3) from the plane of the other four atoms of the six-membered piperazine ring are 0.6066(1) and -0.6332(1) Å, respectively. The two ethyl groups, at N2 and N3, adopt an anti conformation. The furan ring (C12-C13-C14-C15-O4) is planar with a maximum deviation of 0.0296(1)Å. The dihedral angle between the piperazine ring and the furan ring is 142.4(1)°.

CONCLUSIONS

In this study, new piperazine derivatives were obtained by the reaction of S-substituted-3-nitro-1,3-butadienes with some piperazine derivatives in CHCl₃ at room temperature. The substitution reaction proceeds by an addition-elimination mechanism (nucleophilic vinylic substitution (SNVin). 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. The novel piperazine derivatives were obtained in good yields, and are soluble in organic solvents such as chloroform, petroleum ether. The crystal structure of compound 5d was solved by X-ray diffraction method. The crystal structure showed that piperazinyl-substituted-3-nitrobutadienes were E-isomers.

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6. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-1544558 for 5d. Copies of the data can be obtained free of charge, via www.ccdc.cam.ac.uk /conts/retrieving. html or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

Z. Gokmen et al.: Synthesis and spectral properties of new piperazine derivatives and a structural study

Sинтез и спектрални свойства на нови пиперазинови произведения и структурен анализ

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(Резюме)

Синтезирани са нови производи на пиперазина чрез реакции на S-заместени-3-нитро-1,3-бутадиени с някои произведения на пиперазина: (1-(2-фурил)-, 1-(4-флуоробензил)-, 1-(3-флуоробензил)- и 1-(1-тетрахидро-2-фурил) пиперазин) в CHCl₃ при стайна температура. Структурите на новите съединения са охарактеризирани чрез микроанализ, FT-IR, масштабметрия, ¹H- и ¹³C-NMR. Кристалната структура на синтезираното съединение 5d е определена по метода на рентгеновата дифракция. Съединението 5d кристализира в монооклинна пространствена група P2₁/c с a = 12.5503(2) Å, b = 11.2039(2) Å, c = 14.1007(4) Å, Z = 4. Структурата е определена чрез директен метод (SIR92) и е прецизирана спрямо остатъчен индекс R₁ = 0.031.