The Reactions of Some Alkyl(thio)-Substituted 2-Nitrodienes with Piperazines and a Structural Study

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Thiosubstituted nitrodiene compound **1a** was obtained from 2-nitropentachlorobutadiene and dodecanethiol. Compound **1b** was prepared from 2-nitropentachlorobutadiene and hexadecanethiol. Monosubstituted diene compounds **1a** and **1b** reacted with piperazines such as derivatives of **2** and **4** in CH_2Cl_2 and gave the novel compounds. 2-Nitro-3,4,4-trichloro-1-dodecylthio-1-(2-fluorophenyl-piperazinyl]-1,3-butadiene (**3d**) was synthesized and its crystal structure was determined.

Key words: Thiosubstituted Nitrodiene, *N,S*-Substituted Nitrodienes, Piperazine Derivatives

Introduction

In recent years, some mono-, di-, tris(thio)-substituted compounds were obtained from the reactions of nitrodienes with thiols and dithiols [1 – 9]. *N,S*-substituted diene compounds were prepared by the reactions of some mono(thio)-substituted compounds with some amines (primary amine, piperazine, morpholine, piperidine, *etc.* [10 – 15]). The piperazine and piperidine compounds have been submitted to medicinal applications and gen transfer studies due to their interesting biological activity and chemical effects [16 – 20]. According to an US patent, some thiosubstituted dienes also exhibit high biological activity [21].

Nitrodienes, and especially their halogen derivatives, were used to develop preparative methods for the synthesis of complex polyfunctional derivatives of different classes. 2-Nitropentachloro-1,3-butadiene is a very reactive compound. In a substitution reaction proceeding by the addition-elimination reactions [22], a 1-chloro substituent is easily replaced with *N*- and *S*-nucleophiles.

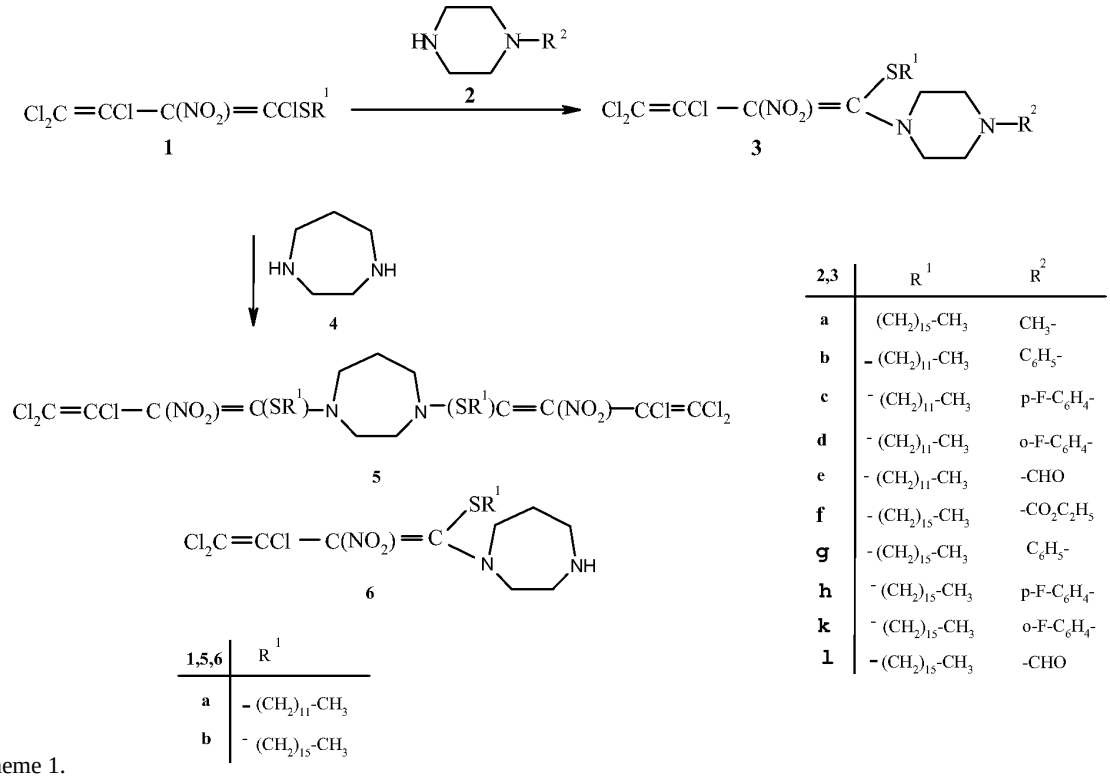
The aim in this study was to synthesize and characterize new *N,S*-subtituted nitrodiene compounds and to determine the crystal structure of one representative product.

Results and Discussion

2-Nitro-1,3,4,4-tetrachloro-1-(dodecylthio)-1,3-butadiene (**1a**) and the hexadecylthio analogue **1b** [12] reacted with the piperazine derivatives **2a – f** to give the new compounds **3a – l**. Novel compounds **5a** and **6b** were obtained from the reaction of **1a, b** with perhydro-1,4-diazepane.

In the IR spectrum of compound **5a** no band is observed in the region 3200 – 3450 cm^{-1} attributable to the streching vibration of a NH group, indicating the formation of 1,4-disubstituted homopiperazine. In contrast, the IR spectrum of **6b** showed a characteristic >NH band at 3450 cm^{-1}. Microanalysis and further spectroscopic data verify these structures. The IR spectra showed a characteristic >C=O band at 1720 cm^{-1} for **3e, 3f** and at 1700 cm^{-1} for **3l**.

The aromatic protons are observed as multiplet at $\delta = 6.9 - 7.4$ ppm for compounds of **3b – d**, and **3g – k**. In the ^1H NMR spectra of the novel compounds containing the piperazine ring (**3a – l**), the piperazine protons are observed as broad singlets at $\delta = 3.16 - 3.84$ ppm for **3a – d** and **3f – l**, and as multiplets at 3.55 – 3.86 ppm for **3e**. In the APT spectra of **3c, d, f, h, k** the CH_2 signals of the piperazine ring are identified in the range 49.46 – 62.34 ppm, the aromatic ring carbon atoms at 114.83 – 127.11 ppm, and the C=O peak is observed at 169.92 ppm for **3f**. In the APCI mass spectrum **5a** the molecular ion peak is observed at $m/z = 901.8$. The major fragment of compound **5a** was observed at $m/z = (M\text{-}46)$, corresponding most likely to $[NO_2]^+$. The obtained products were stable and some of them are yellow in color.



2,3	R^1	R^2
a	$(CH_2)_{15}$-CH_3	CH_3-
b	- $(CH_2)_{11}$-CH_3	C_6H_5-
c	- $(CH_2)_{11}$-CH_3	p-F-C_6H_4-
d	- $(CH_2)_{11}$-CH_3	o-F-C_6H_4-
e	- $(CH_2)_{11}$-CH_3	-CHO
f	- $(CH_2)_{15}$-CH_3	$-CO_2C_2H_5$
g	- $(CH_2)_{15}$-CH_3	C_6H_5-
h	- $(CH_2)_{15}$-CH_3	p-F-C_6H_4-
k	- $(CH_2)_{15}$-CH_3	o-F-C_6H_4-
l	- $(CH_2)_{15}$-CH_3	-CHO

1,5,6	R^1
a	- $(CH_2)_{11}$-CH_3
b	- $(CH_2)_{15}$-CH_3

Scheme 1.

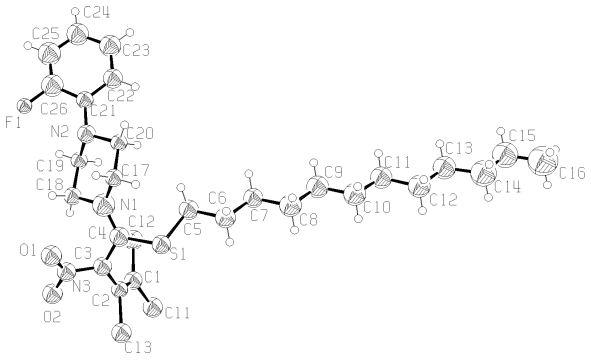


Fig. 1. The molecular structure of compound **3d**. (ORTEP-III [26]) Displacement ellipsoids are plotted at the 50% probability level.

X-ray crystal structure of **3d**

The structure of the compound **3d** is shown in Fig. 1. It contains the expected *N*,*S*-substituted butadienyl skeleton. Selected bond geometry values are given in Table 2. The X-ray analysis of **3d** reveals that chlorine substitution at C4 has occured in the C4 atom. The butadiene moiety assumes a configuration close to cisoid.

Table 1. Crystallographic data and structure refinement for **3d**.

Sum formula	$C_{26}H_{37}N_3O_2Cl_3FS$
M_w [g·mol^{-1}]	581.01
Crystal system	triclinic
Space group	P-1
a [Å]	7.0933
b [Å]	8.3802
c [Å]	27.40930(10)
α [°]	76.418(4)
β [°]	77.526(4)
γ [°]	71.231(4)
V [Å^3]	1481.955(5)
Z	2
$D_{calcd.}$ [g·cm^{-3}]	1.302
μ [cm^{-1}]	4.13
F(000)	612.00
Index ranges, *h*, *k*, *l*	−8/8, −9/9, −32/32
Reflections collected	84762
Independent reflections	5239 [R(int) = 0.140]
Data / restraints / parameters	1447 / 0 /362
Goodness-of-fit on F^2	1.105
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.039$, $wR = 0.044$
Largest diff. peak and hole [e·Å^{-3}]	0.29 and −0.22

In the structure of **3d** the equivalent isotropic displacement coefficients (thermal parameters) of the carbon atoms of the dodecyl chain generally increase

Table 2. Selected bond lengths [Å] and angles [°] with e.s.d. in parentheses for **3d**[a,b].

S1-C4	1.756(5)	C18-C19	1.494(7)
S1-C5	1.801(6)	N1-C4	1.328(6)
C20-C17	1.514(7)	N1-C17	1.474(6)
Cl1-C1	1.724(6)	N2-C19	1.465(6)
C4-C3	1.398(6)	C2-C3	1.448(8)
C2-C1	1.320(9)	N2-C20	1.463(6)
Cl2-C1-C2	122.6(4)	C4-S1-C5	107.9(2)
C4-N1-C18	125.3(4)	C17-N1-C18	112.5(4)
C3-C4-S1	113.4(4)	C3-C4-N1	125.0(5)
S1-C4-N1	121.6(3)	S1-C5-C6	107.2(4)
C20-N2-C19	109.7(4)	N2-C19-C18	109.0(4)
C3-C2-C1	123.0(4)	Cl1-C1-C2	124.0(4)
C1-C2-Cl3	118.9(4)	C4-C3-C2	123.0(5)
C17-C20-N2	111.2(4)	N1-C17-C20	109.7(4)
C4-N1-C17	121.9(4)	Cl2-C1-Cl1	113.4(4)

[a] Average C-C for C(5) to C(16)=1.498(5) Å; [b] average C-C-C for C(5) to C(16)=116.2(4)°.

Table 3. Selected torsion angles of **3d**.

C1-C2-C3-C4	−58.1(7)	N1-C4-C3-C2	139.1(6)
C3-C2-C1-Cl1	179.8(4)	C1-C2-C3- N3	117.8(5)
Cl3-C2-C1-Cl2	−179.0(3)	C18-N1-C17-C20	51.7(6)
C19-N2-C20-C17	61.0(6)		

on going from C5 to C16, reflecting libration of the chain. For C5-C16 of **3d**, the average C-C bond length is 1.498(5) Å and the average C-C-C bond angle is 116.2(4)°. The torsion angles of **3d** are given in Table 3. All of the torsion angles within the dodecyl chain deviate from 180° by less than 1.5°. Thus the C12 chain has a near trans-coplanar conformation. The average deviation from the least-squares plane formed by C5-C16 is 0.040 Å, with a maximum deviation of 0.083 Å for C5. Both the observed values in **3d** are consistent with the corresponding values in a similar compound [28].

The piperazine ring is in the chair conformation. The *o*-fluorophenyl ring is planar with a maximum deviation of 0.007 Å.

Experimental Section

Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were perform with a Carlo Erba 1106 Elemental analyser. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FTIR-8101 spectrometry. NMR spectra were recorded on a Varian^{UNITY} INOVA instrument operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. The mass spectra were obtained on a Finnigan MAX spectrometer in the APCI made.

All chemicals and solvents were obtained commercially and used without purification. Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 63 – 200 μm). TLC plates: silica $60F_{254}$ (Merck, Darmstadt), detection with ultraviolet light (254 nm).

Preparations

General procedure I for preparation of S-substituted polyhalonitrodienes **1a, b** [12]

Equimolar amounts of 1,1,3,4,4-pentachloro-2-nitro-1,3-butadiene in 10 ml of ethanol and thiols in 10 ml ethanol were mixed at r. t. The mixture was stirred for 24 h. Chloroform was added to the reaction mixture. The organic layer was separated and washed with water (4×30 ml) and dried with Na_2SO_4. After the solvent was evaporated the residue was purified by column chromatography on silica gel.

General procedure II for preparation of N, S-substituted polyhalonitrodienes **3a – l, 5a, 6b**

Equimolar amounts of *S*-substituted polyhalonitrodienes **1a, b** and piperazine derivatives **2a – f** or perhydro-1,4-diazepane (**4**) were mixed in dichloromethane at r. t. The mixture was stirred for 2 – 3 h. Chloroform was added to the reaction mixture. The organic layer was separated and washed with water (4×30 ml) and dried with Na_2SO_4. After the solvent was evaporated the residue was purified by column chromatography on silica gel. The yellow crystals of **3d** suitable for X-ray diffraction were obtained by recrystallization by slow evaporation of ethanol at 20 °C.

*3,4,4-Trichloro-1-(dodecylthio)-2-nitro-1-(4-phenylpiperazin-1-yl)-1,3-butadiene (***3b***)*

Yield: 0.14 g (35%). – M.p. 62 – 63 °C. $R_f = 0.67$ (CH_2Cl_2). – IR (KBr): υ = 2800, 2900, 3050 (C-H), 1580, 1620 (C=C), 1300, 1540 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): $\delta = 7.33$ (m, 2 H, N-H_{arom}), 6.96 (m, 3 H, H_{arom}), 3.84 (s, br, 4 H, H_{piper}), 3.36 (s, br, 4 H, H_{piper}), 3.0 (t, $J = 7.08$ Hz, 2 H, SCH_2), 1.7 (m, $J = 7.32$ Hz, 2 H, SCH_2CH_2), 1.26 – 1.44 (m, 18 H, -$(CH_2)_{9-}$), 0.9 (t, $J = 6.84$ Hz, 3 H, CH_3). – $C_{26}H_{38}SO_2N_3Cl_3$ (563.03): calcd. C 55.46, H 6.80, N 7.46; found C 55.02, H 6.29, N 7.14.

*3,4,4-Trichloro-1-(dodecylthio)-1-[4-(4-fluorophenyl)piperazin-1-yl]-2-nitro-1,3-butadiene (***3c***)*

Yield: 0.16 g (40%). Oil. $R_f = 0.21$ ($CHCl_3$). – IR (KBr): υ = 2800, 2900, 3100 (C-H), 1580, 1620 (C=C), 1300, 1505 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): $\delta =$ 6.96 (m, 2 H, F-H_{arom}), 6.84 (m, 2 H, N-H_{arom}), 3.72 (s, br, 4H, H_{piper}), 3.16 (s, br, 4H, H_{piper}), 2.90 (t, $J = 7.08$ Hz, 2 H, SCH_2), 1.60 (m, $J = 7.32$ Hz, 2 H, SCH_2CH_2), 1.16 – 1.34 (m, 18 H, -$(CH_2)_{9-}$), 0.80 (t, $J = 6.84$ Hz, 3 H, CH_3). – ^{13}C NMR (125.68 MHz, $CDCl_3$): $\delta = 14.33$ (CH_3), 22.91, 28.93, 29.26, 29.55, 29.60, 29.74, 29.83, 30.02, 32.13,

35.83 (CH_2), 50.73, 53.29 (NCH_2), 116.09, 116.26, 119.01, 119.07 (CH_{arom}), 125.00, 127.01 (C_{arom}), 118.75, 146.74, 157.33, 159.25 (C_{butad}). – $C_{26}H_{37}N_3SFO_2Cl_3$ (581.02): calcd. C 53.74, H 6.41, N 7.23; found C 53.55, H 5.80, N 7.14.

*3,4,4-Trichloro-1-(dodecylthio)-1-[4-(2-fluorophenyl)piperazin-1-yl]-2-nitro-1,3-butadiene (***3d***)*

Yield: 0.17 g (43%). – M. p. 79 – 80 °C. R_f = 0.52 ($CHCl_3$). – IR (KBr): υ = 2800, 2900, 3050 (C-H), 1580, 1620 (C=C), 1290, 1505 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 6.94 – 7.12 (m, 4 H, H_{arom}), 3.84 (s, br, 4 H, H_{piper}), 3.26 (s, br, 4 H, H_{piper}), 3.10 (t, J = 7.32 Hz, 2 H, SCH_2), 1.70 (m, J = 7.32 Hz, 2 H, SCH_2CH_2), 1.24 – 1.44 (m, 18 H, -$(CH_2)_{9-}$), 0.90 (t, J = 6.84 Hz, 3 H, CH_3). – ^{13}C NMR (125.68 MHz, $CDCl_3$): δ = 14.34 (CH_3), 22.91, 28.93, 29.26, 29.56, 29.61, 29.74, 29.84, 30.02, 32.13, 35.81 (CH_2), 50.60, 53.63 (N-CH_2), 116.63, 116.79, 118.65, 119.61 (CH_{arom}), 124.91, 127.11(C_{arom}), 138.74, 138.82, 155.03, 156.99 (C_{butad}). – $C_{26}H_{37}N_3SO_2FCl_3$ (581.02): calcd. C 53.74, H 6.41, N 7.23; found C 53.06, H 5.92, N 6.96.

*3,4,4-Trichloro-1-(dodecylthio)-1-(4-formylpiperazin-1-yl)-2-nitro-1,3-butadiene (***3e***)*

Yield: 0.14 g (40%). Oil. R_f = 0.36 [CH_2Cl_2/CCl_4(1:1)]. – IR (KBr): υ = 2900, (C-H), 1560, 1610 (C=C), 1200, 1560 cm^{-1} (NO_2), 1720 (C=O). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 3.55 – 3.86 (m, 8 H, H_{piper}), 2.93 (t, J = 7.32 Hz, 2 H, SCH_2), 1.64 (m, J = 7.32 Hz, 2 H, SCH_2CH_2), 1.24 – 1.37 (m, 18 H, -$(CH_2)_{9-}$), 0.86 (t, J = 6.84 Hz, 3 H, CH_3). – $C_{21}H_{34}N_3O_3SCl_3$ (514.94): calcd. C 55.46, H 6.80, N 7.46; found. C 55.02, H 6.29, N 7.14.

*1,4-Bis[3,4,4-trichloro-1-(dodecylthio)-2-nitro-1,3-butadienyl]perhydro-1,4-diazepane (***5a***)*

Yield: 0.20 g (33%). Oil. R_f = 0.45 (CH_2Cl_2). – IR (KBr): υ = 2990, (C-H), 1560, 1605 (C=C), 1280, 1505 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 3.60 (m, 6 H, $H_{homopiper}$), 2.96 (s, br, 4 H, $H_{homopiper}$), 2.65 (t, J = 7.56 Hz, 4 H, 2 SCH_2), 1.65 (m, J = 7.32 Hz, 4 H, 2 SCH_2CH_2), 1.20 – 1.33 (m, 36 H, 2-$(CH_2)_{9-}$), 0.97 (t, J = 6.84 Hz, 6 H, 2 CH_3). – MS (APCI): *m/z* (%) = 901.8 (40) [M^+], 854.95 (14) [M^+-NO_2]. – $C_{37}H_{60}N_4O_4S_2Cl_6$ (901.74): calcd. C 49.28, H 6.70, N 6.21; found C 49.52, H 7.35, N 6.90.

*3,4,4-Trichloro-1-(hexadecylthio)-1-(4-methylpiperazin-1-yl)-2-nitro-1,3-butadiene (***3a***)*

Yield: 0.15 g (47%). Oil. R_f = 0.41 [CH_2Cl_2/EtOAc(1:1)]. – IR (KBr): υ = 2900, (C-H), 1560, 1600 (C=C), 1290, 1540 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 3.74 (s, br, 4 H, H_{piper}), 2.90 (t, J = 7.32 Hz, 2 H, SCH_2), 2.62 (s, br, 4 H, H_{piper}), 2.44 (s, 3 H, N-CH_3) 1.65 (m, J = 7.32 Hz, 2 H, SCH_2CH_2), 1.20 – 1.40 (m, 26 H, -$(CH_2)_{13}$-), 0.88 (t, J = 6.84 Hz, 3 H, CH_3). – $C_{25}H_{44}N_3O_2Cl_3S$ (557.07): calcd. C 56.55, H 7.11, N 6.59; found C 56.59, H 6.73, N 6.81.

*3,4,4-Trichloro-1-(4-ethoxycarbonylepiperazin-1-yl)-1-(hexadecylthio)-2-nitro-1,3-butadiene (***3f***)*

Yield: 0.21 g (52%). Oil. R_f = 0.38 (CH_2Cl_2). – IR (KBr): υ = 2990 (C-H), 1560, 1610 (C=C), 1250, 1520 cm^{-1} (NO_2), 1700 (C=O). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 4.12 (q, J = 7.08 Hz, 2 H, OCH_2), 3.57 (s, br, 8 H, H_{piper}) 2.89 (t, J = 7.08 Hz, 2 H, SCH_2), 1.60 (m, J = 7.32 Hz, 2 H, SCH_2CH_2), 1.20 – 1.40 (m, 26 H, -$(CH_2)_{13}$-), 0.80 (t, J = 6.84 Hz, 3 H, CH_3). – ^{13}C NMR (125.68 MHz, $CDCl_3$): δ = 14.32, 14.82 (CH_3), 22.90, 28.93, 29.24, 29.57, 29.59, 29.73, 29.82, 29.87, 29.89, 29.90, 29.95, 32.14, 35.80, 43.47, (CH_2), 53.07, 62.34 (N-CH_2), 119.16, 125.12, 126.84, 155.30 (C_{butad}), 169.92 (C=O). – $C_{27}H_{46}N_3SO_4Cl_3$ (615.19): calcd. C 52.72, H 7.53, N 6.83; found C 52.32, H 7.93, N 6.41.

*3,4,4-Trichloro-1-(hexadecylthio)- 2-nitro-1-(4-phenylpiperazin-1-yl)-1,3-butadiene (***3g***)*

Yield: 0.09 g (26%). – M. p. 60 – 61 °C. R_f = 0.48 ($CHCl_3$). – IR (KBr): υ = 2900, 3050 (C-H), 1580, 1610 (C=C), 1290, 1540 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 7.28 (m, 2 H, N-H_{arom}), 6.92 (m, 2 H, H_{arom}), 3.80 (s, br, 4 H, H_{piper}), 3.31 (s, br, 4 H, H_{piper}), 2.96 (t, J = 7.08 Hz, 2 H, SCH_2), 1.65 (m, J = 7.32 Hz, 2 H, SCH_2CH_2), 1.20 – 1.40 (m, 26 H, -$(CH_2)_{13}$-), 0.86 (t, J = 6.84 Hz, 3 H, CH_3). – $C_{30}H_{46}N_3O_2SCl_3$ (619.14): calcd. C 58.19, H 7.48, N 6.78; found C 57.94, H 7.43, N 6.76.

*3,4,4-Trichloro-1-[4-(4-fluorophenyl)piperazin-1-yl]-1-(hexadecylthio)-2-nitro-1,3-butadiene (***3h***)*

Yield: 0.22 g (26%). – M. p. 64 – 65 °C. R_f = 0.22 ($CHCl_3$). – IR (KBr): υ = 2800, 3050 (C-H), 1560, 1620 (C=C), 1290, 1505 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 6.96 (m, 2 H, F-H_{arom}), 6.87 (m, 2 H, N-H_{arom}), 3.77 (s, br, 4 H, H_{piper}), 3.21 (s, br, 4 H, H_{piper}), 2.95 (t, J = 7.08 Hz, 2 H, SCH_2), 1.64 (m, J = 7.32 Hz, 2 H, SCH_2CH_2), 1.17 – 1.40 (m, 26 H, -$(CH_2)_{13}$-), 0.86 (t, J = 6.84 Hz, 3 H, CH_3). – ^{13}C NMR (125.68 MHz, $CDCl_3$): δ = 13.09 (CH_3), 21,67, 27.69, 28.02, 28.34, 28.36, 28.50, 28.59, 28.64, 28.67, 28.68, 28.79, 30.91, 34.58, (CH_2), 49.46, 52.09 (N-CH_2), 114.83, 115.00, 117.71, 117.77 (CH_{arom}), 123.75, 125.77 (C_{arom}), 117.70, 145.60, 56.03, 157.94 (C_{butad}). –

$C_{30}H_{45}N_3O_2SCl_3F$ (637.13): calcd. C 56.55, H 7.11, N 6.59; found C 56.13, H 6.60, N 6.77.

*3,4,4-Trichloro-1-[4-(2-fluorophenylpiperazin-1-yl)]-1-(hexadecylthio)-2-nitro-1,3-butadiene (***3k***)*

Yield: 0.14 g (38%). – M. p. 89 – 90 °C. $R_f = 0.27$ ($CHCl_3$). – IR (KBr): $\upsilon = 2900$, 3050 (C-H), 1560, 1620 (C=C), 1290, 1540 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): $\delta = 6.90 - 7.24$ (m, 4 H, H_{arom}), 3.79 (s, br, 4 H, H_{piper}), 3.21 (s, br, 4 H, H_{piper}), 2.96 (t, $J =$ 7.32 Hz, 2 H, SCH_2), 1.65 (m, $J = 7.32$ Hz, 2 H, SCH_2CH_2), 1.17 – 1.40 (m, 26 H, -$(CH_2)_{13}$-), 0.86 (t, $J = 6.84$ Hz, 3 H, CH_3). – ^{13}C NMR (125.68 MHz, $CDCl_3$): $\delta = 14.33$ (CH_3), 22.92, 28.94, 29.27, 29.59, 29.61, 28.50, 29.75, 29.84, 29.89, 29.91, 29.92, 30.02, 32.16, 35.80 (CH_2), 50.60, 53.63 (N-CH_2), 116.64, 119.59, 123.98, 124.87 (CH_{arom}), 118.66, 124.91, (C_{arom}), 127.08, 138.74, 155.04, 157.00 (C_{butad}). – $C_{30}H_{45}N_3O_2SCl_3F$ (637.13): calcd. C 56.55, H 7.11, N 6.59; found C 56.59, H 6.73, N 6.81.

*3,4,4-Trichloro-1-(4-formylpiperazin-1-yl)-1-(hexadecylthio)-2-nitro-1,3-butadiene (***3l***)*

Yield: 0.16 g (47%). – M. p. 128 – 129 °C. $R_f = 0.63$ (CH_2Cl_2/CCl_4). – IR (KBr): $\upsilon = 2900$ (C-H), 1560, 1610 (C=C), 1200, 1560 cm^{-1} (NO_2). – ^{1}H NMR (499.83 MHz, $CDCl_3$): $\delta = 3.60 - 3.86$ (m, 8 H, H_{piper}), 2.90 (t, $J =$ 7.32 Hz, 2 H, SCH_2), 1.65 (m, $J = 7.32$ Hz, 2 H, SCH_2CH_2), 1.13 – 1.41 (m, 26 H, -$(CH_2)_{13}$-), 0.86 (t, $J = 6.84$ Hz, 3 H, CH_3). – $C_{25}H_{42}N_3O_3SCl_3$ (571.05): calcd. C 52.58, H 7.41, N 7.35; found C 51.93, H 6.62, N 7.73.

*3,4,4-Trichloro-1-(hexadecylthio)-2-nitro-1-(perhydro-1,4-diazepanyl)-1,3-butadiene (***6b***)*

Yield: 0.20 g (33%). – M. p. 124 – 125 °C. $R_f = 0.43$ (CCl_4/CH_2Cl_2 1:1). – IR (KBr): $\upsilon = 2900$, (C-H), 1560, 1650 (C=C), 1200, 1530 cm^{-1} (NO_2), 3450 (N-H). – ^{1}H NMR (499.83 MHz, $CDCl_3$): $\delta = 3.69$ (m, 6 H, $H_{homopiper}$), 2.89 (s, br, 4 H, $H_{homopiper}$), 2.61 (t, $J = 7.32$ Hz, 2 H, SCH_2), 1.60 (m, $J = 7.32$ Hz, 2 H, SCH_2CH_2), 1.19 – 1.38 (m, 26 H, -$(CH_2)_{13}$-), 0.81 (t, $J = 6.84$ Hz, 3 H, CH_3). – $C_{25}H_{44}N_3O_2SCl_3$ (557.07): calcd. C 53.90, H 7.96, N 7.54; found C 54.62 H 8.70, N 7.08.

X-ray structure determination of **3d**

Data collection was carried out on a Rigaku R-Axis Rapid-S diffractometer with graphite monochromatized Mo-K_α radiation ($\lambda = 0.71093$ Å). Experimental conditions are summarized in Table 1. The structure was solved by SIR 92 [23] and refined with CRYSTALS [24]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model. The H atom displacement parameters were restricted to be $1.2U_{eq}$ of the parent atom. All calculations were performed using a crystallographic software package [25]. Selected bond distances and bond angles for **3d** are listed in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-267314 for **3d** [27].

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