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The novel *N*, *S*-substituted nitro dienes from the reactions of some mono(alkylthio)-substituted 2-nitrodienes with piperazine and thiomorpholine and a structural study

Cemil Ibis* & N Gulsah Deniz

Istanbul University, Faculty of Engineering, Department of Chemistry 34320 Avcilar-Istanbul, Turkey

E mail: ibiscml@istanbul.edu.tr

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Thiosubstituted nitrodien compounds **1a-f** are obtained from 2-nitropentachlorobutadiene and some alifatic thiols. Compounds **1a-f** have reacted with thiomorpholine **2** and yielded **3a-f** in CH_2Cl_2. The compounds **5a-f** have been obtained by the reactions of **1a-f** with *N*-(diphenylmethyl)piperazine **4** in CH_2Cl_2. 2-Nitro-3,4,4-trichloro-1-(ethylthio)-1-[4-(1-diphenylmethyl)-piperazin-1-yl]-1,3-butadiene **5a** is synthesized and its crystal structure is determined. The compound **5a** crystallizes in the orthorhombic crystal system (space group $P2_12_12_1$) with the unit cell parameters a = 9.4240(2) Å, b = 14.4007(2) Å, c = 18.1891(2) Å, α, β, γ = 90°, V = 2468.48(7) Å^3, Z = 4. The structure has been solved by direct methods (SIR92) and refined to the residual index R_1 = 0.078.

Keywords: Thiosubstituted nitrodiene, *N*,S-substituted nitrodiene, thiomorpholine, piperazine derivatives

IPC: Int.Cl.[8] C07D

It is known that monoaryl- and diarylpiperazines are important for clinical chemistry.[1-3] Some piperazine compounds were used in gen transfer reactions.[4] Some quaternary piperazinium salts show spasmolytic, anthelmintic, or germicidal activities. Polycationic ligands, including piperidine and piperazine rings, exhibit a substantial degree of selective RNA binding.[5] The same thioethers are obtained in the reactions of hexachlorobutadiene with methanethiol. It was reported in the US-patent that these compounds exhibit biological activity.[6]

It has been reported been before S-**,** N-**,** S,S-**,** S,S,S-**,** N,S-substituted diene compounds were obtained from the reaction of nitrodienes with thiols, dithiols and piperazines.[7-13]

Nitrodienes, and especially their halogen derivatives were used to develop preparative methods for the synthesis of complex polyfunctional derivatives of different classes. 2-Nitrohalodiene and mono(thio)-substituted nitrodiene are very reactive compounds. N- and S-nucleophiles easily replace with the chlorine of the nitrovinyl group in 2-nitro-1,3-halodiene by the addition-elimination mechanism.[14]

The aim in this study was to synthesize and characterize new *N*-,S-subtituted nitrodiene compounds.

Result and Discussion

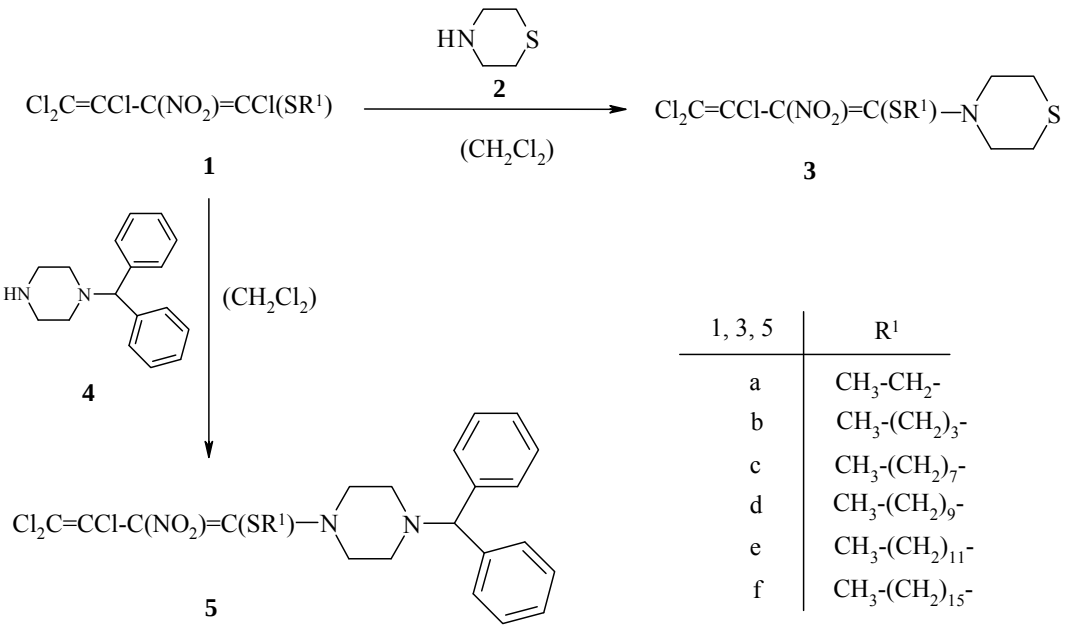
The known polyhalogenated organic compounds were synthesized and used as starting materials. These compounds are 2-nitropentachloro-1,3-butadiene and some mono(thio)substituted nitrodienes **1a-f**. In the second step, **1a-f** gave new compounds **3a-f** with thiomorpholine **2** and **5a-f** with n-(diphenylmethyl)-piperazine **4** (**Scheme I**).

The ^{1}H NMR spectra of **5a-f** showed the piperazine ring, the piperazine protons are observed as broad singlets between 2.5, 3.6 ppm. ^{1}H NMR spectrum of **3a-f** showed thiomorpholine ring as triplet at 2.7 ppm and broad singlet at 3.8 ppm.

^{1}H NMR spectrum of –CH< proton is observed as singlet at 4.2 ppm for **5a-f** compounds. ^{13}C NMR spectrum of –CH< is observed 77.11 ppm for **5a**.

In the APCI mass spectrum of the compound **5a** the respective molecular ion peak is observed at *m/z* = 513.87. Major fragment of compound **5a** was found at *m/z* = (M-35.5). It is likely that this corresponds to the chlor ion [Cl]$^+$. Compound **3b** showed a molecular ion peak at *m/z* = 392.94. Major fragment of compound **3b** was found at *m/z* = 346.94 [M-NO_2]$^+$.

The obtained products were stable and some of them are yellow in colour. Structure of these new



1, 3, 5	R^1
a	CH_3-CH_2-
b	CH_3-$(CH_2)_3$-
c	CH_3-$(CH_2)_7$-
d	CH_3-$(CH_2)_9$-
e	CH_3-$(CH_2)_{11}$-
f	CH_3-$(CH_2)_{15}$-

Scheme I

products were characterized by microanalysis, spectroscopic methods and single crystal structure of compound **5a** is determined by X-ray diffraction method.

X-ray Study

The structure of the compound **5a** is shown in **Figure 1**. It contains the expected N,S-substituted butadienyl skeleton. The X-ray analysis of the **5a (Tables I** and **II)** has revealed that chlorine atoms elimination has occured in the C_4 atom. The butadiene unit has assumed a configuration close to cisoid, but is not completely planar as would be if the two double bounds were fully conjugated.

In the compound **5a**; the C-C bond lenghts of the butadiene chain are 1.329(3), 1.453(3) and 1.401(3) Å respectively for C_1-C_2, C_2-C_3 and C_3-C_4. The torsional angle of the carbon skeleton in the skew s-*cis* structure is 56.80° (**Table III**). Both the observed values in **5a** are consistent with the corresponding values in the similar compounds.[23-25]

In the structure of **5a** thermal parameters of the carbon atoms of the ethyl chain generally increase on going from C5 to C6 (**Table IV**).

The both phenyl rings are planar with a maximum deviations of 0.0017 Å (plane 1 = C12-C13-C14-C15-C16-C17) and 0.0044 Å (plane 2 = C18-C19-C20-C21-C22-23). The piperazine ring is in chair conformation and planar with a maximum deviation of 0.239 Å (plane 3 = N2-C7-C8-C9-C10-N3). 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 -0.134(1) and 0.199(2) Å. The planar phenyl rings are inclined at an angle of 77.92°(1). Dihedral angles are 69.34°(1) between planes 1 and 3, 99.12°(1) between planes 2 and 3.

The molecule packing diagram for compound **5a** is shown in **Figure 2** as a projection along a-axis. The common motif is the typical herring-bone arrangement in compound **5a**.

Experimental Section

Melting points were measured on a Buchi B-540 melting point apparatus and uncorrected. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FTIR-8101 spectrometry. UV spectra were recorded in UV-VIS spectrophotometer TU-1901. ^{1}H NMR and ^{13}C NMR spectra were recorded on a VarianUNITYINOVA operating at 500 MHz. Mass spectra were obtained on a Thermo Advantage MAX LC/MS/MS spectrometer according to APCI. Crystal structure of **5a** was determined on Rigaku R-Axis Rapid-S X-Ray Single Crsytal diffractometer. Products were isolated by column chromatography on Silica gel (Fluka silica gel 60, particle size 63-200 μm). TLC plates silica $60F_{254}$ (Merck, Darmstadt) and detection was carried out with ultraviolet light (254 nm).

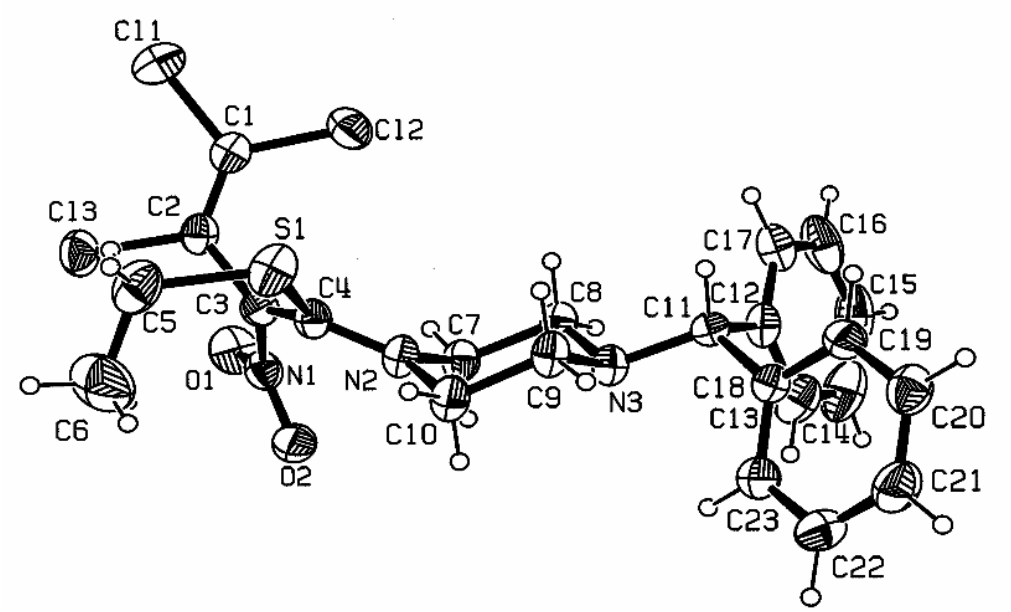


Figure 1 — The molecular structure of compound **5a**. Displacement ellipsoids are plotted at the 30% probability level (Symmetry transformations used to generate equivalent atoms: (i)- x, -y, -z).

Table I — Crystallographic data and structure refinement for **5a**

Sum formula	$C_{23}H_{24}N_3O_2SCl_3$
f_w (g.mol^{-1})	512.88
Space group	$P2_12_12_1$ (No. 19)
	a =9.4240(2) Å
	b =14.4007(2) Å
	c =18.1891(2) Å
	α, β, γ =90^0
Vol [Å^3]	2468.48(7)
Z	4
D_{calc}(g.cm^{-3})	1.380
μ [cm^{-1}] 4.13	
F(000)	1064.00
Index ranges	-13<=h<=13
	-20<=k<=20
	-25<=l<=25
Reflections collected	145722
Independent reflections	4083 (R_{int} = 0.026)
Data / restraints / parameters	3988 / 0 /313
Goodness-of-fit on F^2 1.083	
Final R indices [$I>2\sigma(I)$]	R =0.030, wR = 0.078
Largest diff. peak and hole	0.52 and -0.26 e·Å^{-3}

Synthesis of S-Substitued Polyhalonitrodienes 1a-f (ref. 14-18) : Equimolar amounts of 1,1,3,4,4-pentachloro-2-nitro-1,3-butadiene and thiols in 10 mL dichloromethane were mixed at room temperature. The mixture was stirred for 24 hr. 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.

Synthesis of N,S-Substitued polyhalonitrodienes 3a-f and 5a-f: Equimolar amounts of *S*-substituted polyhalonitrodienes, thimorpholine and *N*-(diphenyl-methyl)-piperazine were mixed in dichloromethane at room temp. The mixture was stirred for 24 hr. 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 **5a** suitable for X-Ray diffraction were obtained on recrystalyzation by slow evaporation of the ethanol at the room temperature.

Crystallography

A yellow crystal of $C_{23}H_{24}N_3O_2SCl_3$ **5a** having approximate dimensions of 0.30 × 0.20 × 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation (λ = 0.71093 Å). The data were collected at a temperature of 20 ± 1°C to a maximum 2θ value of 60.2°. Experimental conditions are summarized in **Table I**.

The structure was solved by SIR 92 (ref. 19). and refined with CRYSTALS.[20] The non-hydrogen atoms

Table II — Selected bond lengths [Å] and angles [°] with e.s.d. in parentheses for **5a**

Cl3-C2	1.744(2)	Cl2-C1	1.717(2)	C4-S1-C5	105.6(1)
Cl1-C1	1.711(2)	S1-C4	1.760(2)	C1-C2-C3	122.9(2)
S1-C5	1.809(3)	O1-N1	1.237(3)	C4-C3-C2	123.6(2)
O2-N1	1.238(3)	N3-C11	1.487(3)	C6-C5-S1	116.0(3)
N3-C9	1.464(3)	N3-C8	1.467(3)	N1-C3-C2	115.3(2)
N2-C4	1.328(3)	N2-C10	1.465(3)	N2-C7-C8	109.2(2)
N2-C7	1.476(3)	N1-C3	1.410(3)	Cl2-C1-C2	122.1(2)
C3-C4	1.401(3)	C1-C2	1.329(3)	C10-C9-N3	111.0(2)
C2-C3	1.453(3)	C18-C11	1.523(3)	S1-C4-N2	114.9(1)
C18-C19	1.396(4)	C18-C23	1.371(4)	N3-C11-C18	111.4(2)
C11-C12	1.531(3)	C12-C17	1.386(3)	C3-N1-O1	118.5(2)
C12-C13	1.386(3)	C17-C16	1.379(3)	C11-N3-C8	109.1(2)
C9-C10	1.525(3)	C8-C7	1.516(3)	C4-N2-C10	123.0(2)
C16-C15	1.364(4)	C19-C20	1.405(5)	C3-C2-Cl3	118.2(2)
C13-C14	1.392(4)	C23-C22	1.397(4)	Cl2-C1-Cl1	113.6(1)
C14-C15	1.365(4)	C5-C6	1.472(5)	Cl1-C1-C2	124.3(2)
C22-C21	1.358(5)	C21-C20	1.365(6)	C21-C22-C23	119.8(3)

Table III — Selected torsion angles for **5a**

C1-C2-C3-C4	56.8(3)	C4-S1-C5-C6	51.6(3)
C5-S1-C4-C3	41.4(2)	N2-C4-C3-C2	-144.6(2)
N3-C9-C10-N2	56.5(2)	S1-C4-C3-C2	27.3(3)
C3-C2-C1-Cl1	-170.8(2)	Cl3-C2-C3-C4	-120.1(2)
Cl3-C2-C1-Cl1	6.1(3)	C10-N2-C4-S1	-150.5(2)
N3-C8-C7-N2	-60.3(2)	N3-C11-C12-C17	-148.6(2)
Cl3-C2-C3-N1	59.0(3)	C10-N2-C4-S1	-150.5(2)
C17-C12-C13-C14	-0.7(4)	C18-C19-C20-C21	-0.5(5)
Cl3-C2-C3-C4	-120.1(2)	Cl3-C2-C1-Cl2	-174.4(2)

were refined anisotropically. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.95 Å), and refined using a riding model. The H atom displacement parameters were restricted to be $1.2U_{eq}$ of the parent atom. The maximum electron-density peak is located 0.60 Å from atom Cl1. Selected bond distances and bond angles for **5a** are listed in **Table II.** ORTEP-III view of the molecular structure of **5a** is given in **Figure 1** and **Figure 2** (ref. 21). 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-600381 for **5a** (ref 22).

2-Nitro-3, 4, 4-trichloro-1-(ethylthio)-1-(thiomorpholinyl)-1,3-butadiene **3a**. Yield 0.182 g (51%); m.p.: 128-29°C. R_f ($CHCl_3$): 0.25; IR (KBr): 2900 (C-H), 1580, 1630 (C=C), 1290, 1510 cm^{-1}(C-NO_2); UV-vis ($CHCl_3$): 242, 397 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 1.28 (t, J = 7.32 Hz, 3H, CH_3), 2.92 (t, J = 7.32 Hz, 2H, S-CH_2), 2.72 (t, 4H, $H_{thiomorp}$), 3.8 (s, br,

Table IV — Atomic coordinates(x10^4) and equivalent isotropic displacement (x10^3) for **5a**

Atom	x	y	z	U(eq)[a]
Cl1	5926.9(8)	2302.8(6)	2765.9(4)	82.5(2)
Cl2	6158.4(7)	2885.6(4)	4269.1(4)	68.8(2)
Cl3	7284.2(8)	371(5)	3151.0(3)	75.7(2)
S1	4248.9(7)	755.4(6)	4872.6(4)	72.2(2)
O1	9486(2)	805.7(13)	4346.2(10)	75.5(6)
N1	8514(2)	628(1)	4780.4(11)	56.7(5)
N2	6248(2)	1127.4(12)	5823.7(9)	51.7(5)
N3	6051(2)	2211.5(13)	7139.7(9)	50.4(5)
C1	6408(2)	2009(2)	3642.7(12)	56.6(6)
C2	6920(2)	1184(2)	3836.0(11)	50.8(6)
C3	7125(2)	911(2)	4597.4(12)	50.1(6)
C4	6038(2)	909(2)	5122.8(11)	48.3(5)
C5	4252(3)	-147(2)	4181(2)	82.8(9)
C6	5007(5)	-1007(2)	4375(3)	122(2)
C7	5320(3)	845(2)	6438.4(12)	58.5(7)
C8	4826(2)	1705(2)	6846.4(12)	55.4(6)
C9	6924(2)	2516(2)	6519.5(12)	50.5(6)
C10	7451(2)	1688(2)	6074.3(12)	52.6(6)
C11	5539(2)	3006(1)	7589.1(11)	46.4(6)
C12	4756(2)	2665(2)	8275.4(11)	49.2(6)

[a] Equivalent isotropic U defined as one-third of the trace of the ortogonalized U_{ij} tensor.

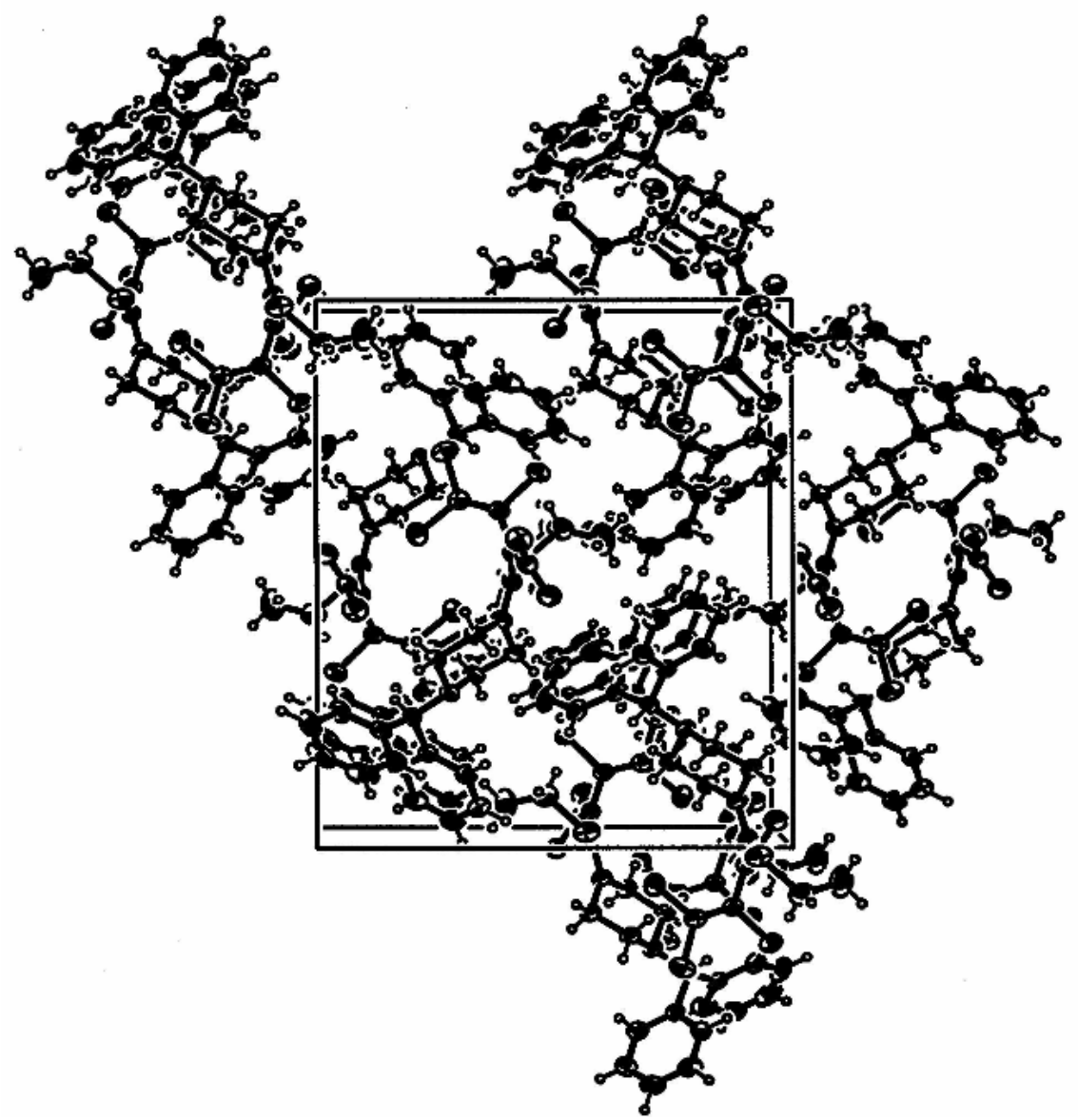


Figure 2 — Packing diagram of **5a;** molecular overlap view from the a-axis

4H, $H_{thiomorp}$); $C_{10}H_{13}N_2O_2S_2Cl_3$ (M, 363.71). Calcd. C, 33.02; H, 3.60; N, 7.70. Found: C, 33.73; H, 3.81; N, 7.40.

2-Nitro-3,4,4-trichloro-1-(ethylthio)-1-[4-(1-diphenylmethyl)-piperazin-1-yl]-1,3-butadiene **5a**: Yield 0.180 g (53%); m.p.: 161-62°C. R_f ($CHCl_3$): 0.25; IR (KBr): 2900 (C-H), 1580, 1630 (C=C), 1290, 1520 (C-NO_2), 3100 cm^{-1} (=C-H_{arom}); UV-vis ($CHCl_3$): 241, 392 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.33 Hz, 3H, CH_3), 2.85 (t, *J* = 7.32 Hz, 2H, S-CH_2), 2.5 (s, br, 4H, H_{piper}), 3.6 (s, br, 4H, H_{piper}), 4.2 (s, 1H, CH), 7.0-7.4 (m, 10H, $H_{arom.}$); ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 15.22 (CH_3), 30.01 (S-CH_2), 46.95, 53.71 (N-CH_2), 77.11 (-CH<), 127.15, 128.02, 128.70 (**C**H_{arom}), 141.81 (**C**$_{arom}$), 118.32, 126.82, 132.68, 168.64 (C_{butad}); MS (+APCI): *m/z* 513.87 (M^+), 478.37 (M^+-Cl); $C_{23}H_{24}N_3O_2S_1Cl_3$ (M, 512.89). Calcd. C, 53.86; H, 4.72; N, 8.19. Found: C, 54.10; H, 4.85; N, 8.10.

2-Nitro-3, 4, 4-trichloro-1-(butylthio)-1-(thiomorpholinyl)-1,3-butadiene **3b**: Yield 0.178 g (49%); Oil, R_f ($CHCl_3$): 0.38; IR (KBr): 2900 (C-H), 1580, 1650 (C=C), 1290, 1530 cm^{-1} (C-NO_2). UV-vis ($CHCl_3$): 242, 396 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 7.33 Hz, 3H, CH_3), 1.36 (m, *J* = 7.33 Hz, 2H, CH_2), 1.58 (m, *J* = 7.33 Hz, 2H, S-CH_2-CH_2), 2.88 (t, *J* = 7.32 Hz, 2H, S-CH_2), 2.74 (t, *J* = 5.37 Hz, 4H, $H_{thiomorp}$), 3.8 (s, br, 4H, $H_{thiomorp}$); ^{13}C NMR (125.68

MHz, $CDCl_3$): δ 13.74 (CH_3), 22.10, 28.09, 31.91, 35.36 (CH_2), 45.67, 56.24 ($C_{thiomorp}$), 119.20, 124.99, 126.93, 170.91 ppm (C_{butad}); MS (+APCI): *m/z* 392.94 (M^+), 346.94 (M^+-NO_2); $C_{12}H_{17}N_2O_2S_2Cl_3$ (M, 391.77). Calcd. C, 36.79; H, 4.37; N, 7.15. Found: C, 36.25; H, 4.35; N, 7.09.

2-Nitro-3,4,4-trichloro-1-(butylthio)-1-[4-(1-diphenylmethyl)-piperazin-1-yl]-1,3-butadiene **5b**: Yield 0.301 g (60%); m.p.: 114-15°C. R_f ($CHCl_3$): 0.28; IR (KBr): 2900 (C-H), 1590, 1650 (C=C), 1290, 1530 (C-NO_2), 3100 cm^{-1} (=C-H_{arom}); UV-vis ($CHCl_3$): 242, 392 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.33 Hz, 3H, CH_3), 1.32 (m, *J* = 7.33 Hz, 2H, CH_2), 1.5 (m, *J* = 7.33 Hz, 2H, S-CH_2-C*H*$_2$), 2.85 (t, *J* = 6.84 Hz, 2H, S-CH_2), 2.5 (s, br, 4H, H_{piper}), 3.6 (s, br, 4H, H_{piper}), 4.2 (s, 1H, CH), 7.0-7.4 (m, 10H, H_{arom}); $C_{25}H_{28}N_3O_2S_1Cl_3$ (M, 540.94); Calcd. C, 55.51; H, 5.22; N, 7.77. Found: C, 54.93; H, 5.15; N, 7.50.

2-Nitro-3, 4, 4-trichloro-1-(octylthio)-1-(thiomorpholinyl)-1,3-butadiene **3c**: Yield 0.148 g (42%); Oil, R_f ($CHCl_3$): 0.43; IR (KBr): 2900 (C-H), 1580, 1650 (C=C), 1290, 1530 cm^{-1} (C-NO_2). UV-vis ($CHCl_3$): 245, 397 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 6.84 Hz, 3H, CH_3), 1.1-1.4 (m, 10H, -$(CH_2)_5$-), 1.6 (m, 2H, S-CH_2-C*H*$_2$), 2.87 (t, *J* = 7.33 Hz, 2H, S-CH_2), 2.7 (t, *J* = 5.37 Hz, 4H, $H_{thiomorp}$), 3.8 (s, br, 4H, $H_{thiomorp}$); ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 14.29 (CH_3), 22.81, 28.09, 29.23, 29.35, 2.90, 31.92, 35.71 (CH_2), 45.34, 56.23 ($C_{thiomorp}$), 119.22, 126.76, 130.26, 170.92 (C_{butad}); MS (+APCI): *m/z* 448.99 (M^+); $C_{16}H_{25}N_2O_2S_2Cl_3$ (M, 447.88); Calcd. C, 42.91; H, 5.63; N, 6.25. Found: C, 42.95; H, 5.60; N, 6.26.

2-Nitro-3,4,4-trichloro-1-(octylthio)-1-[4-(1-diphenylmethyl)-piperazin-1-yl]-1,3-butadiene **5c**: Yield 0.242 g (52%); Oil, R_f ($CHCl_3$): 0.35; IR (KBr): 2900 (C-H), 1590, 1630 (C=C), 1290, 1530 (C-NO_2), 3100 cm^{-1} (=C-H_{arom}). UV-vis ($CHCl_3$): 243, 391 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 7.32 Hz, 3H, CH_3), 1.1-1.4 (m, 10H, -$(CH_2)_5$-), 1.55 (m, *J* = 7.33 Hz, 2H, S-CH_2-C*H*$_2$), 2.85 (t, *J* = 6.84 Hz, 2H, S-CH_2), 2.5 (s, br, 4H, H_{piper}), 3.6 (s, br, 4H, H_{piper}), 4.2 (s, 1H, CH), 7.0-7.4 (m, 10H, H_{arom}); $C_{29}H_{36}N_3O_2S_1Cl_3$ (M^+, 597.05); Calcd. C, 58.34; H, 6.08; N, 7.04. Found: C, 58.10 ; H, 6.12 ; N, 6.94.

2-Nitro-3, 4, 4-trichloro-1-(decylthio)-1-(thiomorpholinly)-1,3-butadiene **3d**: Yield 0.162 g (47%); Oil, R_f ($CHCl_3$): 0.47; IR (KBr): 2900 (C-H), 1580, 1650 (C=C), 1290, 1530 cm^{-1} (C-NO_2); UV-vis ($CHCl_3$): 245, 396 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 6.84 Hz, 3H, CH_3), 1.1-1.4 (m, 14H, -$(CH_2)_7$-), 1.6 (m, *J* = 7.33 Hz, 2H, S-CH_2-C*H*$_2$), 2.9 (t, *J* = 7.33 Hz, 2H, S-CH_2), 2.7 (t, 4H, $H_{thiomorp}$), 3.8 (s, br, 4H, $H_{thiomorp}$); $C_{18}H_{29}N_2O_2S_2Cl_3$ (M, 475.93); Calcd. C, 45.43; H, 6.14; N, 5.89. Found: C, 45.64 ; H, 6.29 ; N, 5.71.

2-Nitro-3,4,4-trichloro-1-(decylthio)-1-[4-(1-diphenylmethyl)-piperazin-1-yl]-1,3-butadiene **5d**: Yield 0.240 g (53%); Oil, R_f ($CHCl_3$): 0.56; IR (KBr): 2900 (C-H), 1590, 1630 (C=C), 1290, 1530 (C-NO_2), 3100 cm^{-1} (=C-H_{arom}); UV-vis ($CHCl_3$): 243, 393 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 7.33 Hz, 3H, CH_3), 1.1-1.4 (m, 14H, -$(CH_2)_7$-), 1.55 (m, *J* = 7.32 Hz, 2H, S-CH_2-C*H*$_2$-), 2.8 (t, *J* = 7.32 Hz, 2H, S-CH_2), 2.5 (s, br, 4H, H_{piper}), 3.6 (s, br, 4H, H_{piper}), 4.2 (s, 1H, CH), 7.0-7.4 (m, 10H, H_{arom}); $C_{31}H_{40}N_3O_2S_1Cl_3$ (M, 625.11); Calcd. C, 59.57; H, 6.45; N, 6.72. Found: C, 58.85 ; H, 6.65 ; N, 6.69.

2-Nitro-3,4,4-trichloro-1-(dodecylthio)-1-(thiomorpholinyl)-1,3-butadiene **3e**: Yield 0.302 g (87%); Oil, R_f ($CHCl_3$): 0.47; IR (KBr): 2900 (C-H), 1580, 1650 (C=C), 1290, 1530 cm^{-1} (C-NO_2). UV-vis ($CHCl_3$): 246, 397 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 7.32 Hz, 3H, CH_3), 1.1-1.4 (m, 18H, -$(CH_2)_9$-), 1.6 (m, *J* = 7.32 Hz, 2H, S-CH_2-C*H*$_2$-), 2.9 (t, *J* = 7.33 Hz, 2H, S-CH_2), 2.7 (t, *J* = 5.38 Hz, 4H, $H_{thiomorp}$), 3.8 (s, br, 4H, $H_{thiomorp}$); $C_{20}H_{33}N_2O_2S_2Cl_3$ (M, 503.99); Calcd. C, 47.66; H, 6.60; N, 5.56. Found: C, 47.31; H, 6.71; N, 5.60.

2-Nitro-3,4,4-trichloro-1-(dodecylthio)-1-[4-(1-diphenymethyl)-piperazin-1-yl]-1,3-butadiene **5e**: Yield 0.232 g (51%); Oil, R_f ($CHCl_3$): 0.53; IR (KBr): 2900 (C-H), 1590, 1630 (C=C), 1290, 1530 (C-NO_2), 3100 cm^{-1} (=C-$H_{arom.}$); UV-vis ($CHCl_3$): 243, 392 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 7.32 Hz, 3H, CH_3), 1.1-1.4 (m, 18H, -$(CH_2)_9$-), 1.5 (m, 2H, S-CH_2-C*H*$_2$-), 2.8 (t, *J* = 7.32 Hz, 2H, S-CH_2), 2.45 (s, br, 4H, H_{piper}), 3.6 (s, br, 4H, H_{piper}), 4.2 (s, 1H, CH), 7.0-7.5 (m, 10H, H_{arom}); $C_{33}H_{44}N_3O_2S_1Cl_3$ (M, 653.16); Calcd. C, 60.68; H, 6.79; N, 6.43. Found: C, 60.28 ; H, 6.41 ; N, 6.20.

2-Nitro-3, 4, 4-trichloro-1-(hexadecylthio)-1-(thiomorpholinyl)-1,3-butadiene **3f**: Yield 0.126 g (53%); m.p.: 60-61°C. R_f ($CHCl_3$): 0.50; IR (KBr): 2800, 2900 (C-H), 1580, 1630 (C=C), 1280, 1530 cm^{-1} (C-NO_2). UV-vis ($CHCl_3$): 244, 396 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 6.84 Hz, 3H, CH_3), 1.0-1.4 (m, 26H, -$(CsH_2)_{13}$-), 1.58 (m, *J* = 7.32 Hz, 2H, S-CH_2-C*H*$_2$), 2.85 (t, *J*= 7.32 Hz, 2H, S-CH_2), 2.7 (t, *J* = 5.37 Hz, 4H, $H_{thimorp}$), 3.8 (s, br, 4H, $H_{thimorp}$); $C_{24}H_{41}N_2O_2S_2Cl_3$ (M, 560.09); Calcd. C, 51.47; H, 7.38; N, 5.00. Found: C, 51.82 ; H, 7.54 ; N, 5.10.

2-Nitro-3,4,4-trichloro-1-(hexadecylthio)-1-[4-(1-difenilmetil)-piperazin-1-yl]-1,3-butadiene **5f**: Yield 0.138 g (32%); Oil, R_f ($CHCl_3$): 0.56; IR (KBr): 2900 (C-H), 1590, 1650 (C=C), 1280, 1550 (C-NO_2), 3100 cm^{-1} (=C-H_{arom}); UV-vis ($CHCl_3$): 241, 392 nm; ^{1}H NMR (499.83 MHz, $CDCl_3$): δ 0.8 (t, *J* = 6.83 Hz, 3H, CH_3), 1.1-1.3 (m, 26H, -$(CH_2)_{13}$-), 1.55 (m, *J* = 7.33 Hz, 2H, S- CH_2-CH_2), 2.8 (t, *J* = 7.33 Hz, 2H, S-CH_2), 2.5 (s, br, 4H, H_{piper}), 3.6 (s, br, 4H, H_{piper}), 4.2 (s, 1H, CH), 7.1-7.5 (m, 10H, H_{arom}). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ 22.92 (CH_3), 28.77, 28.87, 28.95, 29.13, 29.17, 29.26, 29.48, 29.75, 29.84, 29.88, 29.92, 30.07, 30.62, 32.15, 35.77 (CH_2), 46.66, 53.72 (N-CH_2), 77.05 (-CH<), 128.35, 128.51, 128.69 (CH_{arom}), 141.86 (C_{arom}), 118.18, 126.80, 132.65, 169.06 (C_{butad}); MS (+APCI): *m/z* 710.08 (M^+), 674.58 (M^+-*Cl*); $C_{37}H_{52}N_3O_2S_1Cl_3$ (M, 709.27); Calcd. C, 62.66; H, 7.39; N, 5.92. Found: C, 62.10 ; H, 7.42 ; N, 6.03.

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