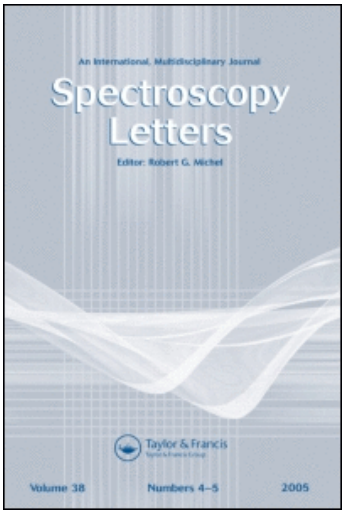


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Crystal Structures of 4-Methyl-1-(3,4,4-trichloro-1-cyclohexylsulfanyl-2-nitro-buta-1,3-dienyl) Piperidine and 4-(3,4,4-Trichloro-1-decylsulfanyl-2-nitro-buta-1,3-dienyl) Morpholine and Spectroscopic Properties

Gökşin Aydınlı[a]; Çiğdem Sayıl[a]; Cemil İbiş[a]
[a] Department of Chemistry, Faculty of Engineering, Istanbul University, Avcılar-İstanbul, Turkey

Online publication date: 19 January 2010

To cite this Article Aydınlı, Gökşin , Sayıl, Çiğdem and İbiş, Cemil(2010) 'Crystal Structures of 4-Methyl-1-(3,4,4-trichloro-1-cyclohexylsulfanyl-2-nitro-buta-1,3-dienyl) Piperidine and 4-(3,4,4-Trichloro-1-decylsulfanyl-2-nitro-buta-1,3-dienyl) Morpholine and Spectroscopic Properties', Spectroscopy Letters, 43: 1, 44 — 50
To link to this Article: DOI: 10.1080/00387010903261131
URL: http://dx.doi.org/10.1080/00387010903261131

Spectroscopy Letters, 43:44–50, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903261131

Taylor & Francis
Taylor & Francis Group

Crystal Structures of 4-Methyl-1-(3,4,4-trichloro-1-cyclohexylsulfanyl-2-nitro-buta-1,3-dienyl) Piperidine and 4-(3,4,4-Trichloro-1-decylsulfanyl-2-nitro-buta-1,3-dienyl) Morpholine and Spectroscopic Properties

Gökşin Aydınlı, Çiğdem Sayıl, and Cemil İbiş

Department of Chemistry, Faculty of Engineering, Istanbul University, Avcılar-İstanbul, Turkey

ABSTRACT 4-Methyl-1-(3,4,4-trichloro-1-cyclohexylsulfanyl-2-nitro-buta-1,3-dienyl) piperidine (**2a**) and 4-(3,4,4-trichloro-1-decylsulfanyl-2-nitro-buta-1,3-dienyl) morpholine (**3b**) were synthesized, and their crystal structures were determined. The compound **2a** is monoclinic, with space group P21/n, $a = 13.2874(8)$, $b = 9.7584(4)$, $c = 15.9479(9)$ Å, $\beta = 109.110(3)°$. $V = 1953.91(18)$ Å^3, $Z = 4$. The cyclohexyl and piperidine rings adopt chair conformation. The compound **3b** is monoclinic, with space group P 1 21/c 1, $a = 15.7741(3)$, $b = 8.9335(10)$, $c = 16.7775(4)$ Å, $\beta = 100.7382(13)°$. $V = 2322.85(8)$Å^3, $Z = 4$. The morpholine ring is in a chair conformation. The butadiene unit assumed a configuration close to cissoid in both structures, and their spectroscopic properties were investigated.

KEYWORDS crystal structure, N,S-substituted nitrodienes, spectroscopic properties, X-ray diffraction

INTRODUCTION

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.). In recent years, some *N,S*-substituted diene compounds have been obtained, and their structures have been determinated.[1–7] However, there are only a few reports on the crystal structure of these compounds.[8–10] The piperazine and piperidine compounds have been subjected to medicinal applications and gen transfer studies due to their interesting biological activity and chemical effects.[11–13] According to a U.S. patent, some thiosubstituted dienes—such as insecticide, herbicide, fungicide—also exhibit high biological activity.[14]

Address correspondence to Çiğdem Sayıl, Department of Chemistry, Faculty of Engineering, Istanbul University, 34320 Avcılar-İstanbul, Turkey. E-mail: sayil@istanbul.edu.tr

Halogen derivatives of nitrobutadienes are suitable model objects for elucidation of the features of nucleophilic vinylic substitution (S_NVin). The preferred primary reaction center of 2-nitroperchloro-1,3-butadiene is the activated terminal carbon atom of the nitrodichlorovinyl moiety. This carbon atom allows for an attack by different nucleophiles in SNVin processes. Under harsher conditions the internal carbon atom is additionally open to the attack of nucleophiles.[15,16]

The goal of the present work was to synthesize and to investigate unknown spectroscopic properties of 4-methyl-1-(3,4,4-trichloro-1-cyclohexylsulfanyl-2-nitro-buta-1,3-dienyl) piperidine (**2a**) and 4-(3,4,4-trichloro-1-decylsulfanyl-2-nitro-buta-1,3-dienyl) morpholine (**3b**). Deep insight into their structural aspects in the solid states and crystallographic analyses of compounds **2a** and **3b** were achieved, and the results are presented in this article.

MATERIALS AND METHODS

Experimental Section

4-Methyl-1-(3,4,4-trichloro-1-cyclohexylsulfanyl-2-nitro-buta-1,3-dienyl) piperidine (**2a**) and 4-(3,4,4-trichloro-1-decylsulfanyl-2-nitro-buta-1,3-dienyl) morpholine (**3b**) (Fig. 1) compounds were prepared according to a method reported earlier[6,7] (Scheme 1).

The title compound **2a**, was synthesized from (1,3,4,4-tetrachloro-2-nitro-buta-1,3-dienyl) cyclohexane,

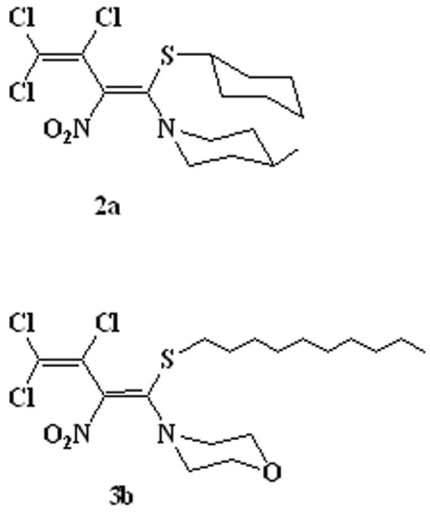
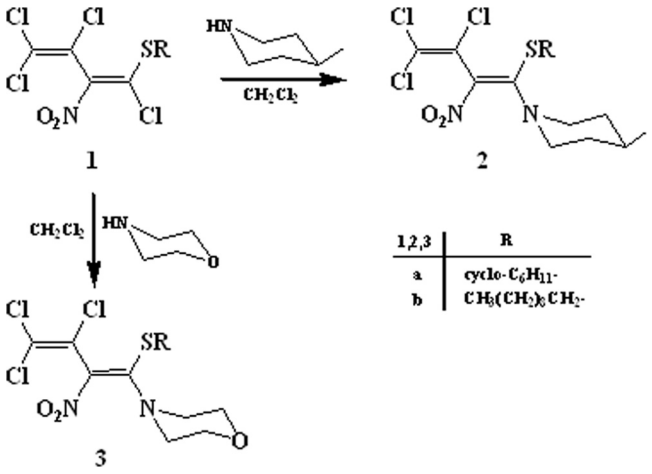


FIGURE 1 The chemical structural diagrams of title compound 2a and 3b.



SCHEME 1 The synthesis route of title compounds.

1a, and 4-methylpiperidine. (1,3,4,4-tetrachloro-2-nitro-buta-1,3-dienyl) cyclohexane (0.50 g, 1.42 mmol) and 4-methylpiperidine (0.14 g, 1.42 mmol) were mixed in diethyl ether (30 ml) at room temperature. The mixture was stirred for 2–3 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. Yellow crystals of **2a** suitable for X-ray diffraction analysis were obtained by slow evaporation of ethanol at room temperature.

3b; 1,3,4,4-Tetrachloro-1-(decylsulfanyl)-2-nitrobuta-1,3-diene (0.20 g, 0.48 mmol), **1b**, and morpholine (0.04 g, 0.48 mmol) were mixed in dichloromethane (25 ml) at room temperature. The mixture was stirred for 2–3 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 had evaporated, the residue was purified by column chromatography on silica gel. Yellow crystals of **3b** suitable for X-ray diffraction analysis were obtained by slow evaporation of ethanol at room temperature.

2a; Yield 69% (0.40 g) m.p. = 131–132°C (EtOH). IR (KBr): $\nu = 3008$, 2936, 2852 cm^{-1} (C–H), 1569 (C=C), 1524,1259 (NO_2). -^{1}H-NMR ($CDCl_3$): $\delta = 3.6$–4.6 ppm (m,1H, S-**CH**), 3.2–3.6 (m, 4H, N-C**H**$_2$), 1.1–1.9 (m, 15H, 7C**H**$_2$, C**H**), 0.9–1.0 (m, 3H, C**H**$_3$). –UV ($CHCl_3$): λ_{max} 293 (lg ε 4.00), 397 nm (4.07). –^{13}C-NMR ($CDCl_3$): 167.3, 126.1, 123.3, 116.6 ppm (**C**$_{butd.}$), 54.3 (S-**C**H), 30.3 (**C**H<),

54.3, 34.6, 29.9, 26.2, 25.5 ($\mathbf{C}H_2$), 14.3 ($\mathbf{C}H_3$). $C_{16}H_{23}Cl_3SN_2O_2$(413.79)-MS (ESI): m/z (%) = 413.10 (100) [M^+].

3b; Yield 62% (0.14 g) m.p. = 75–76°C (EtOH). IR (KBr): ν = 2963, 2924, 2853 cm^{-1} (C−H), 1594 (C=C), 1531, 1261 (NO_2). $-^1$H-NMR ($CDCl_3$): δ = 3.6–3.7 ppm (m, 8H, $-C\mathbf{H}_{2morph.}$), 2.8–2.9 (t, 2H, S-$C\mathbf{H}_2$, J = 7.32 Hz.), 1.2–1.6 (m, 16H, $8CH_2$), 0.8–0.9 (m, 3H, $C\mathbf{H}_3$). –UV ($CHCl_3$): λ_{max} 293 (1 g ε 5.88), 393 nm (5.94). $-^{13}$C-NMR ($CDCl_3$): 131.5, 125.7, 117.3, 108.8 ppm($\mathbf{C}_{butd.}$), 65.4, 52.6, 34.9, 30.8, 28.8, 28.7, 28.3, 28.0, 27.9, 27.7, 21.6 ($\mathbf{C}H_2$), 13.1 ppm($\mathbf{C}H_3$). $C_{18}H_{29}SN_2Cl_3O_3$(459.8) -MS (ESI): m/z (%) = 459.26(100) [M^+].

Spectral Measurements

All chemicals and solvents were obtained commercially and used without purification. TLC was performed on precoated aluminum plates (Silicagel 60 F_{254}; Merck; U.S.). The structures of **2a** and **3b** were determinated by microanalysis and spectroscopic data. Melting points were measured on a Buchi B-540 melting-point apparatus (Switzerland) and uncorrected. Elemental analyses were performed by Carlo Erba 1110 Elemental analyzer (Italy). Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FTIR-8101 spectrometer (Japan). UV spectra were recorded in Perkin Elmer Precisely Lambda 35 UV-VIS spectrometer (U.S.). NMR spectra were recorded on Varian^{UNITY} INOVA instrument (U.S.) operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer (U.S.) using ion-trap mass analyzer for both APCI and ESI sources. Data collection was carried out on a Rigaku R-Axis Rapid-S diffractometer (Japan) with graphite monochromatized Mo-K_α radiation (λ = 0.71093 Å).

Crystallography

Experimental conditions are summarized in Table 1 for **2a** and **3b**. The structures were solved by SIR 92[17] and refined with CRYSTALS.[18] 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 1.2 U_{eq} of the parent atom. All calculations were performed using a crystallographic software package.[19] Selected bond distances and bond angles for **2a** and **3b** are listed in Table 2. Some

TABLE 1 Crystal Data and Structure Refinement for Compounds 2a and 3b

	2a	3b
Sum formula	$C_{16}H_{23}Cl_3N_2O_2S$	$C_{18}H_{29}N_2O_3C1_3S$
M_ω ($g \cdot mol^{-1}$)	413.78	459.86
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	P 21/c
Colour	Yellow	Yellow
a (Å)	13.2874(8)	15.7741(3)
b (Å)	9.7584(4)	8.9335(1)
c (Å)	15.9479(9)	16.7775(4)
β (°)	109.110(3)	100.7382(13)
V[Å^3]	1953.91	2322.85(8)
Z	4	4
$D_{calcd.}$ ($g.cm^{-3}$)	1.407	1.315
μ [cm^{-1}]	0.587	0.504
F(000)	864.00	968.00
Index ranges, *h, k, l*	$-15 <= h <= 15, -11 <= k <= 11$	$-22 <= h <= 22, -12 <= k <= 12$
	$-19 <= l <= 18$	$-21 <= l <= 23$
θ range for data collection (°)	2.5–25.0	3.0–30.5
Reflections collected	65702	137612
Independent reflections	3450 [*R*(int) = 0.117]	7203[*R*(int) = 0.030]
Goodness-of-fit on F^2	0.951	1.210
Final *R* indices [$I > 2\sigma$(I)]	*R*=1.034,*wR*= 0.176	*R* = 0.0740,wR = 0.0250
Largest diff. peak and hole	0.69 and −0.77 e. Å^{-3}	0.36 and −0.34 e. Å^{-3}

TABLE 2 Selected Bond Lengths [Å] Angles and Angles [°] With ESD in Parentheses for 2a and 3b

2a			
C11-C1	1.719(7)	C13-C2	1.755(6)
C12-C1	1.727(6)	S1-C4	1.750(5)
S1-C5	1.840(7)	O1-N1	1.259(7)
O2-N1	1.233(7)	N1-C3	1.425(7)
N2-C4	1.337(8)	N2-C15	1.475(8)
N2-C11	1.476(7)	C3-C4	1.404(7)
C3-C2	1.427(7)	C2-C1	1.329(7)
C4-S1-C5	106.3(3)	C3-N1–O1	115.7(5)
C3-N1-O2	121.3(5)	O1-N1-O2	123.0(5)
C4-N2-C15	123.3(4)	C4-N2-C11	125.5(5)
C15-N2-C11	111.1(5)	C4-C3-C2	122.7(4)
C4-C3-N1	120.1(4)	C2-C3-N1	117.2(5)
S1-C4-N2	114.9(4)	S1-C4-C3	122.5(4)
3b			
S1-C4	1.750(1)	S1-C9	1.828(2)
C13-C2	1.736(1)	C11-C1	1.723(2)
C12-C1	1.705(1)	O2-N1	1.241(1)
O1-N1	1.237(1)	N2-C4	1.344(1)
N2-C8	1.466(1)	N2-C5	1.469(1)
O3-C7	1.414(2)	O3-C6	1.423(2)
C4-C3	1.390(1)	C2-C3	1.456(1)
C2-C1	1.320(2)		
C4-S1-C9	104.44(6)	C4-N2-C8	122.55(9)
C4-N2-C5	123.90(9)	C8-N2-C5	112.75(9)
C7–03-C6	109.8(1)	C3-C4-S1	114.78(8)
C3-C4-N2	124.15(9)	S1-C4-N2	121.06(7)
C3-C2-C1	123.6(1)	C3-C2-CB	117.24(9)
C1-C2-C13	119.1(1)	N1-C3-C4	121.88(9)

TABLE 3 Selected Torsion Angles [°] With ESD in Parentheses for 2a and 3b

2a	
C5-S1-C4-N2	148.0(3)
C5-S1-C4-C3	−39.8(4)
C4-S1-C5-C6	−68.2(5)
C4-S1-C5-C10	170.3(4)
O1-N1-C3-C4	167.5(5)
O1-N1-C3-C2	−12.0(8)
O2-N1-C3-C4	−14.8(8)
O2-N1-C3-C2	165.7(6)
C15-N2-C4-S1	150.4(3)
C15-N2-C4-C3	−21.8(7)
C11-N2-C4-S1	−26.2(6)
C11-N2-C4-C3	161.6(4)
C4-N2-C15-C14	−117.8(5)
C11-N2-C15-C14	59.3(5)
C4-C3-C2-C1	−54.6(8)
3b	
C9-S1-C4-N2	−45.0(1)
C9-S1-C4-C3	134.23(8)
C4-S1-C9-C10	−124.47(9)
C8-N2-C4-S1	158.29(8)
C8-N2-C4-C3	−20.9(2)
C5-N2-C4-S1	−32.7(1)
C6-O3-C7-C8	63.1(1)
C7-O3-C6-C5	−60.1(1)
S1-C4-C3-C2	−33.6(2)
N2-C4-C3-C2	145.6(1)
N2-C4-C3-N1	−35.8(2)
C1-C2-C3-C4	−67.1(2)

torsion angles are given in Table 3. ORTEP-III views of the molecular structure of title compounds are given in Fig. 2 and Fig. 3, and crystal packing diagrams are in Fig. 4 and Fig. 5.[20] The final fractional atomic coordinates are given in Table 4 for **3b**. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-694814 for **2a** and CCDC-694815 for **3b.**[21]

RESULTS AND DISCUSSION

X-Ray Structure Determination

The title compounds contain the expected *N,S*-substituted butadienyl skeleton. The X-ray analysis of **2a** and **3b** reveal that chlorine substitution at C4 has occurred in the C4 atom. The butadiene unit assumes a configuration close to cissoid. The configuration about the double bonds in butadiene moiety has been firmly secured by X-ray crystallography. The structure of title compounds are shown in Fig 2. They

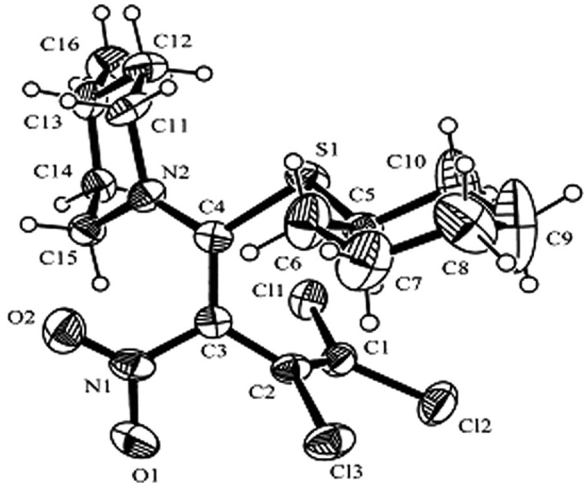


FIGURE 2 The molecular structure of the title compound 2a. Displacement ellipsoids are plotted at the 50%-probability level.

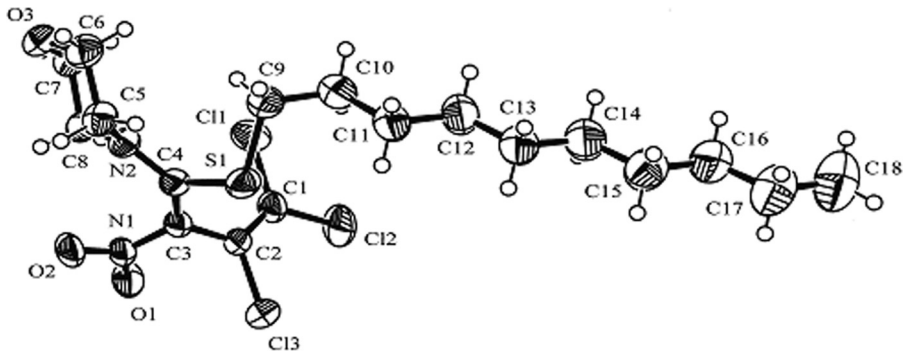


FIGURE 3 **The molecular structure of the title compound 3b. Displacement ellipsoids are plotted at the 50%-probability level.**

were subsequently shown to have *E*-geometry about the C4 double bonds in both compounds. The C−C bond lengths of the butadiene moiety of **2a** are 1.404(7), 1.427(7), and 1.329(7) Å for C3-C4, C3-C2 and C2-C1, respectively. The C−C bond lengths of the butadiene chain agree well with corresponding distances in a similar compound.[22] Torsion angle of C4-C3-C2-C1 is −54.6(8)°. The cyclohexyl and piperidine rings adopt normal chair conformation. Weak C−H−N and C−H−S interactions between neighboring piperidine and cyclohexyl rings help to stabilize the crystal structure.

The structure of **3b** contains linear alkyl chain structure. The alkyl substituent has a fully extended conformation. The U_{eq} values of the C atoms of the decyl chain generally increase on going from C9 to C18 (Table 4), reflecting libration of the chain. For the chain C9-C18, the average C−C bond length is 1.489(4) Å, and the average C−C−C angle is 116.9(2)°. All the torsion angles within the decyl chain deviate from 180° by less than 2.4°. Thus, the C10 chain has a near transcoplanar conformation. The observed values are consistent with the corresponding values in a similar compound.[9] The morpholine ring is in a chair conformation. The C−C bond lengths of the butadiene unit are 1.390(1), 1.456(1), and 1.320(2) Å for C3−C4, C3−C2, and C2−C1, respectively.[8,24] Torsion angle of C4−C3−C2−C1 is −67.1(2)°. In solid-state structure of **3b**,

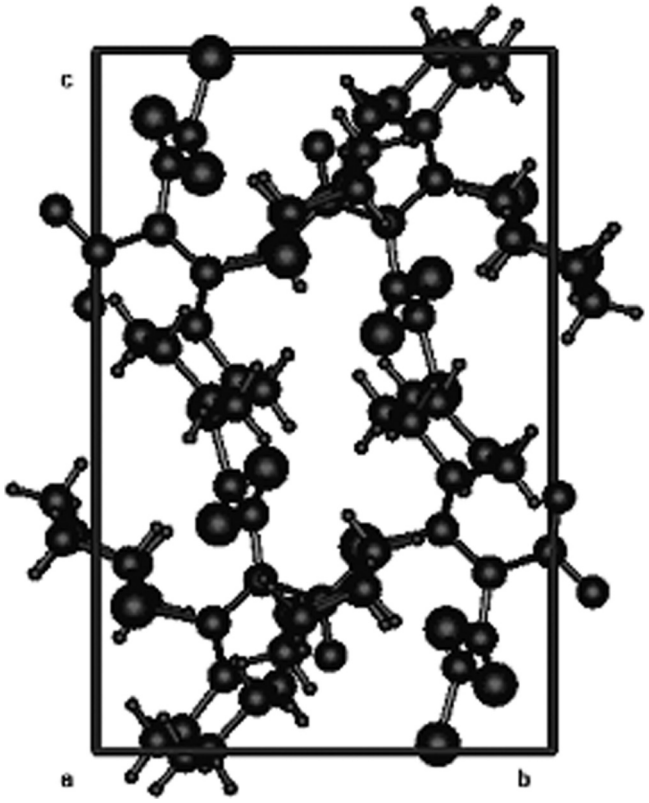


FIGURE 4 **Unit-cell packing diagram for compound 2a, with molecular overlap view from the *a* axis, and with 30% ellipsoid excluding H atoms.**

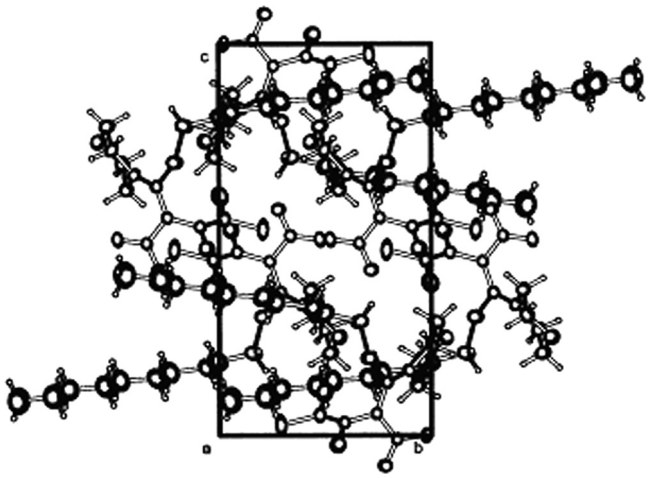


FIGURE 5 **Unit-cell packing diagram for compound 3b, with molecular overlap view from the *a* axis, and with 30% ellipsoid excluding H atoms.**

TABLE 4 Atomic Coordinates and Temperature Factors (Å^2) for 3b

Atom	X	Y	Z	B_{eq}
S1	0.22420(2)	0.29365(4)	0.80270(2)	4.048(7)
C13	0.23612(2)	0.44268(4)	1.02381(2)	4.791(8)
C11	0.43908(3)	0.50476(4)	0.88992(3)	5.563(9)
C12	0.34562(3)	0.70908(4)	0.97364(3)	6.313(10)
O2	0.35975(7)	0.02439(8)	0.99989(5)	4.83(2)
O1	0.38832(7)	0.21836(10)	1.07704(5)	4.82(2)
N2	0.35936(6)	0.10337(10)	0.83425(5)	3.26(2)
O3	0.46692(7)	−0.06491(10)	0.75069(6)	4.82(2)
N1	0.36215(7)	0.16211(10)	1.00960(6)	3.50(2)
C1	0.36063(9)	0.52772(12)	0.94792(8)	3.85(3)
C2	0.31623(8)	0.41242(12)	0.96730(7)	3.26(2)
C3	0.33037(7)	0.25885(11)	0.94389(6)	3.07(2)
C4	0.31279(7)	0.20817(12)	0.86417(6)	3.11(2)
C5	0.32301(8)	−0.0027(1)	0.76999(7)	4.06(3)
C6	0.38272(10)	−0.0236(2)	0.71019(8)	4.86(3)
C7	0.50123(8)	0.0483(2)	0.80638(8)	4.38(3)
C8	0.44826(8)	0.0668(1)	0.87232(7)	3.69(3)
C9	0.26209(10)	0.3385(2)	0.70898(8)	5.08(3)
C10	0.25115(10)	0.5032(2)	0.68891(10)	5.76(4)
C11	0.16075(10)	0.5618(2)	0.67286(10)	5.35(4)
C13	0.06697(11)	0.7957(2)	0.64533(11)	6.21(4)
C12	0.15464(11)	0.7272(2)	0.66031(11)	6.02(4)
C15	−0.01886(12)	1.0393(2)	0.62617(13)	7.06(5)
C14	0.06506(11)	0.9651(2)	0.64011(12)	6.67(5)
C16	−0.02001(12)	1.2056(2)	0.61771(12)	6.84(5)
C17	−0.1054(1)	1.2788(3)	0.6008(2)	8.97(7)
C18	−0.1078(2)	1.4417(3)	0.5906(2)	10.53(8)

$B_{eq} = 8/3\ \pi^2(U_{11}\ (aa^*)^2 + U_{22}(bb^*)^2 + U_{33}\ (cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$.

molecule is held together in ways by C−H...N and C−H...S interactions.

The experimental results have shown that the bond lengths and torsion angles of butadiene moiety in both compounds were slightly different. They were affected by the substituents in both compounds.

NMR and UV-Visible Spectra

The IR and ^{1}H-NMR spectra of title compounds have already been studied, but no reports have been published on the UV-visible and ^{13}C-NMR spectra. The structures of title compounds were confirmed also by ^{13}C-NMR APT spectrums in the present study. Four quaternary carbon atoms of butadienyl moieties of **2a** and **3b** resonated at δ_c 108.8–167.3. In the APT spectrum of **3a**, the CH_2 and CH peaks of morpholine and piperidine rings are identified at δ_c 54.3, 34.6, 29.9, 26.2, 25.5 and δ_c 54.3, 30.3. In addition only one C signal of CH_3 group appeared at δ_c 14.3. All CH_2 protons of compound **3b** are observed at δ_c 65.4, 52.6, 34.9, 30.8, 28.8, 28.7, 28.3, 28.0, 27.9, 27.7, 21.6.

TABLE 5 UV–Vis Absorption Data for Compounds 2a and 3b

	λ_{max} in nm (logε)		
	n-Hexane	$CHCl_3$	DMF
2a	380(4.79)	397(4.07)	390(4.45)
	290(4.80)	293(4.00)	264(4.55)
3b	376(6.00)	393(5.94)	388(6.43)
	287(6.10)	293(5.88)	263(6.25)

The absorption spectra of compounds **2a** and **3b** were measured in the nonpolar n-hexane and in the polar solvents $CHCl_3$ and DMF. The molar absorption coefficients were determined in the solvents, and the data are presented in Table 5. Experimental results showed that generally the λ_{max} value of title compounds' shifts were absorbed at longer wavelengths in polar solvents $CHCl_3$ and DMF than in nonpolar solvent n-hexane (Fig. 6).

Furthermore, some characteristic bands in the IR spectra of compounds **2a** and **3b** were mentioned. The C=C stretching band is observable at 1569, 1594 cm^{-1}, and the NO_2 groups are observable at 1524, 1531 cm^{-1} (asymmetric stretching) and at 1259, 1261 cm^{-1} (symmetric stretching). Note

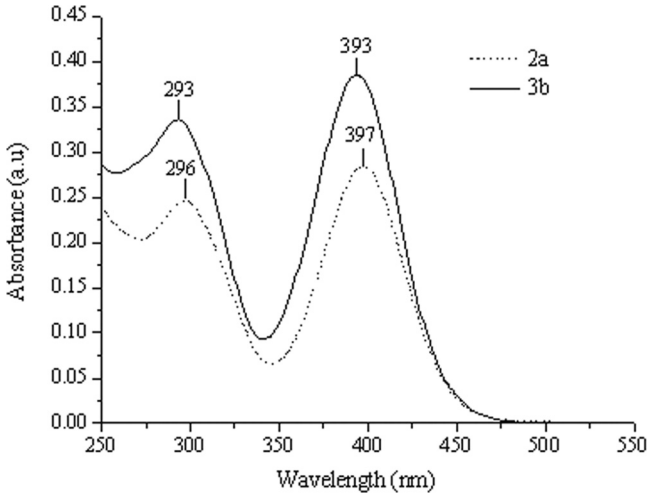


FIGURE 6 UV-Vis absorption spectra of 2a and 3b in $CHCl_3$.

that our spectroscopic data are in accordance with those that have been reported in related articles.[6,7]

ACKNOWLEDGMENTS

This work was supported by the Research Fund of the University of Istanbul.

REFERENCES

1. Ibis, C.; Gokmen, Z. S,N-substituted dienes and S,N-substituted trienes from mono(thio)-substituted 2-nitrodiene compounds. *Phosphorus Sulfur and Silicon* **1998**, *143*, 67–75.
2. Ibis, C.; Yilmaz, N. New N,S-substituted diene compounds from reactions of mono(arylthio)-substituted polyhalo-2-nitrodienes with amines. *Phosphorus Sulfur and Silicon* **2000**, *159*, 87–98.
3. Ibis, C.; Sayil, C. New N-, S-substituted nitrodienes from reactions of primary and secondary amines with mono(thio) substituted nitrodienes. *Rev. Roum. Chim.* **2001**, *46*, 211–216.
4. Ibis, C.; Aydinli, G. Synthesis of dibutadienyl piperazines, 1,1-dithio and 1,4-dithio substituted dienes from nitrodienes. *Phosphorus Sulfur and Silicon* **2002**, *177*, 2529–2535.
5. Ibis, C.; Onul, M. Some new N,S-substituted 2-nitrodiene compounds from relations of mono(p-fluorarylthio)substituted dienes with amines. *Phosphorus Sulfur and Silicon* **2003**, *178*, 1881–1889.
6. Ibis, C.; Goksel, F. S.; Aydinli, G. New N,S-substituted dienes from the reactions of some aliphatic mono(thio)-substituted nitrodienes with aromatic primary amines and cyclic amines. *Phosphorus Sulfur and Silicon* **2003**, *178*, 777–783.
7. Ibis, C.; Aydinli, G. Einige Neue, S,S- und S,N-substituierte 1,3-nitrodienverbindungen. *Sulfur Letters* **1999**, *23*(2), 67–77.
8. Ibis, C.; Sayil, M. C.; Deniz, N. G. 1,3,4,4-Tetrachloro-4-(4-chlorophenyl-sulfanyl)-2-nitrobuta-1,3-diene. *Acta Cryst.* **2006**, *E62*, o800–o801.
9. Ibis, C.; Sayil, M. C.; Ozkok, F. 3,4,4-Trichloro-1-[4-(2-fluorophenyl) piperazinyl]-1-(n-hexadecylsulfanyl)-2-nitrobuta-1,3-diene. *Acta Cryst.* **2006**, *E62*, o1147–o1148.
10. Aydinli, G.; Sayil, C.; Ibis, C. 2,4,4-Tris(benzylsulfanyl)-1,1-dichloro-3-nitrobuta-1,3-diene. *Acta Cryst.* **2009**, *E65*, o272–o273.
11. Nishiyama, M.; Yamamoto, T.; Koie, Y. Synthesis of N-arylpiperazines from aryl halides and piperazine under a palladium tri-tert-butylphosphine catalyst. *Tetrahedron Lett.* **1998**, *39*, 617–620.
12. Kerrigan, F.; Martin, C.; Thomas, G. H. Synthesis of arylpiperazines via palladium-catalysed aromatic amination reactions of bromoarenes with N-tert-butoxycarbonylpiperazine. *Tetrahedron Lett.* **1998**, *39*, 2219–2222.
13. Solodin, I.; Heath, T. D. Synthesis of amphiphilic piperidinium derivatives: Cationic lipids. Part 4. *Synlett* **1996**, *7*, 619.
14. Henry, B. Polyunsaturated sulfides and sulfones and method of preparing same. U.S. Patent US3021370, February 13, 1962. (Diamond Alkali Co.)
15. Kaberdin, R. V.; Potkin, V. I.; Zapol'skii, V. A. Nitrobutadienes and their halogen derivatives: Synthesis and reactions. *Russ. Chem. Rev.* **1997**, *66*(10), 827–842.
16. Zapol'skii, V. A.; Namyslo, J. C.; Gjikaj, M.; Kaufmann, D. E. Chemistry of polyhalogenated nitrobutadienes, 4: Reactions of mono-, bis-, and tris(4-tolylthio) derivatives of 2-nitroperchloro-1,3-butadiene with alpha, beta-bifunctional nucleophiles. *ARKIVOC* (Gainesville, FL, U.S.) **2007**, *i*, 76–93.
17. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. SIR92: A program for automatic solution of crystal structures by direct methods. *J. Appl. Cryst.* **1994**, *27*, 435–436.
18. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. CRYSTALS version 12: Software for guided crystal structure analysis. *J. Appl. Cryst.* **2003**, *36*, 1487.
19. *CrystalStructure*, version 3.5.1; crystal structure analysis package; Rigaku and Rigaku/MSC: The Woodlands, TX 2000–2003.
20. Farrugia, L. J. ORTEP-3 for Windows: A version of ORTEP-III with a graphical user interface (GUI). *J. Appl. Crystallogr.* **1997**, *30*, 565–566.
21. Further information may be obtained from Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, U.K., by quoting the depository numbers CCDC-694814 for 2a and CCDC-694815 for 3b. E-mail: deposit@ccdc.cam.ac.uk
22. Surange, S. S.; Kumaran, G.; Rajappa, S.; Rajalakshmi, K.; Pattabhi, V. Synthesis and characterization of 1-amino-4-methylthio-2-nitro-1,3-butadienes. *Tetrahedron* **1997**, *53*, 8531–8540.