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Structural Investigation of 3,4,4-Trichloro-1-(4-benzylpiperidine)-1-(2-naphthylthio)-2-nitro-1,3-butadiene

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The compound 3,4,4-trichloro-1-(4-benzylpiperidine)-1-(2-naphthylthio)-2-nitro-1,3-butadiene was synthesized from the reaction of 1,3,4,4-tetrachloro-1-(2-naphthylthio)-2-nitro-1,3-butadiene (**1**) with 1-(4-benzylpiperidine) (**2**) and characterized by elemental analysis, IR spectra, UV spectra, ^{1}H NMR, ^{13}C NMR, MS and X-ray single crystal determination. In the asymmetric unit of the present compound, $C_{26}H_{23}N_2O_2SCl_3$, crystallizes in the orthorhombic space group $Pna2_1$, a = 18.8242(4) Å, b = 9.1910(2) Å, c = 29.4390(6) Å, V = 5093.3(2) Å^3, Z = 8, R_1 = 0.086. The asymmetric unit contains two molecules. The piperidine ring adopts a chair conformation. The butadiene unit was not planar as would be expected if the two double bonds were fully conjugated.

Key Words: Butadiene unit, Crystal structure, Piperidine ring, Chair conformation, Spectroscopy.

INTRODUCTION

The piperidinyl derivatives show an excellent biological activity[1]. Benzylpiperidine compounds which exhibit extremely excellent insecticidal activities do not harm the beneficial insects[2]. The compounds are useful for therapy of cerebral edema, acute symptoms incerebral apoplexy and protection of brain and nerve-cell, or useful as anticholines terase or as brain function-improving agent[3]. The N,S-substituted 1,3-halodiene compounds were prepared from the reactions of some mono(thio)substituted diene with some amines such as primary amine, heterocyclicamine (piperazine, morpholine, piperidine, *etc.*)[4].

With the aim of gaining a deep insight into the structural aspect in the solid state, crystallographic analyses of the 3,4,4-trichloro-1-(4-benzylpiperidine)-1-(2-naphthylthio)-2-nitro-1,3-butadiene (**3**) compound was carried out and the result is presented in this paper.

EXPERIMENTAL

Preparation: 3,4,4-Trichloro-1-(4-benzylpiperidine)-1-(2-naphthylthio)-2-nitro-1,3-butadiene (**3**) compound was prepared according to a method reported earlier[5] (Fig. 1).

Compound 3: 0.1 g (0.25 mmol) 1,3,4,4-tetrachloro-1-(2-naphthylthio)-2-nitro-1,3-butadiene (**1**) and 0.044 g (4-benzyipiperidine) (**2**) were mixed in dry ether at room temperature. The mixture was stirred for 24 h. Then chloroform (30 mL) was added to the reaction mixture. The organic layer

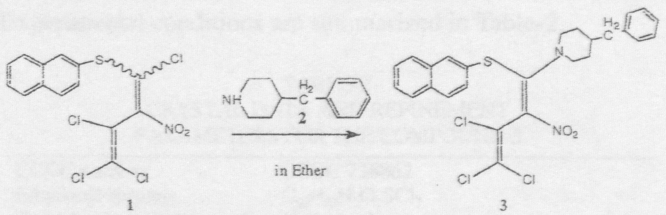
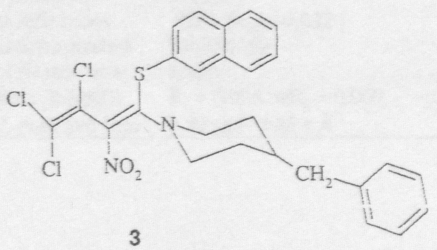


Fig. 1. Synthesis scheme of compound **3**

was separated, washed with water (4 × 30 mL) and dried with anhydrous $MgSO_4$. The solvent was evaporated and the residue was crystallized in ethanol.

All chemicals and solvents were obtained commercially and used without purification. Thin layer chromatography was performed on precoated aluminum plates (silica gel 60 F_{254}, Merck-Merck KGaA, Darmstadt, Germany). The structure of compound **3** (Fig. 2) was determinated by micro-analysis and spectroscopic studies.



3

Fig. 2. Chemical structure of compound 3

Melting points were measured on a Buchi B-540 melting point apparatus (BUCHI Labortechnik, AG, Switzerland) and uncorrected. Elemental analyses were performed by Carlo Erba 1106 elemental analyzer (Strada Rivoltana 20090, Milano, Italy). Infrared spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FTIR-8101 spectrometer (Shimadzu Corporation Analytical Instruments). ^1H and ^{13}C NMR spectra were recorded on VarianUNITY INOVA (Yarian AG NMR Systems Choilerstrasse, 38 Postfach CH-6303 Zug.-Switzerland) operating at 500 MHz (^1H) and 125 MHz (^{13}C). Ultraviolet spectra were recorded on a Beckman DB-GT spectrometry (Beckman Coulter, Inc., 4300 N. Harbor Boulevard, P.O. Box 3100, Fullerton, CA 92834-3100 USA). Mass spectra were obtained using a Finnigan LCQ Advantage Max. LC/MS instrument.

Compound 3: Yield 72 % (0.097) m.p. 138-139 °C (EtOH). $R_f = 0.58$ ($CHCl_3$/petroleum ether 1:1). IR (KBr, ν_{max}, cm^{-1}): 3010, 2980 (C-H), 1590 (C=C), 1510, 1280 (C-NO_2). - ^1H NMR (499.74 MHz, $CDCl_3$, TMS_{int}) δ: 6.8-8.1 (m, 12H, Ar-H), 3.4-4.1 (m, 1H, CH), 3.0-3.3 (m, 4H, $2CH_2$), 1.2-1.8 (m, 4H, $2CH_2$), 2.1-2.3 (m, 2H, CH_2). UV-vis ($CHCl_3$) λ_{max} (nm) (log ε): 389 (4.01), 251 (4.25). ^{13}C NMR (125.66 MHz, $CDCl_3$): 155.4, 138.9, 134.1, 132.1, 131.8, 128.9, 128.1, 128.0, 127.5, 127.3, 127.1, 126.9, 126.7, 126.0, 108.8, 47.8, 41.3, 36.7, 29.9. MS (+ESI): m/z (%) 557 (100) $[M+Na]^+$, 452 (100) $[M-NO_2]^+$ and $[M-Cl]^+$, 498 (71) $[M-Cl]^+$, Anal. $C_{26}H_{23}N_2O_2SCl_3$ (533.908). Calcd. C 58.49; H 4.34; N 5.2; found C 58.72; H 4.18; N 5.18.

The ultraviolet absorption spectra, in the region 190-900 nm were recorded on a a Beckman DB-GT spectrometry in 1.00 cm cell at 25 ± 0.1 °C. The spectra were run in spectra quality solvents (Merck) using concentration of 1×10^{-4} M. UV-Vis spectra of **3** compound was submitted protic solvents in $CHCl_3$, methanol and aprotic solvents in DMF and DMSO. (Fig. 3). Absorption maximum and molar apsorpsitivity of **3** compound was given in Table-1.

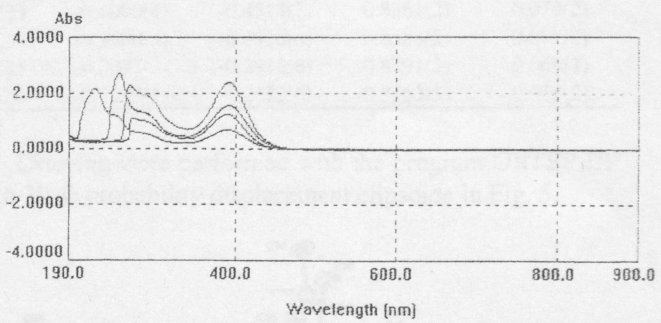


Fig. 3. UV-Vis spectra of **3** compound

TABLE-1
UV-VIS DATA FOR DIFFERENT APROTIC AND PROTIC SOLVENTS OF COMPOUND 3

$CHCl_3$	MeOH	DMF	DMSO
Absorption maxima (λ_{max}) nm			
389	388	387	390
251	220	268	265
Molar absorptivity (log ε) M^{-1} cm^{-1}			
4.01	3.39	3.43	4.15
4.25	3.89	3.38	4.13

The mass spectra of **3** in the positive ion mode for ESI confirmed the proposed structure; molecular peak was identified at m/z 557 (Fig. 4).

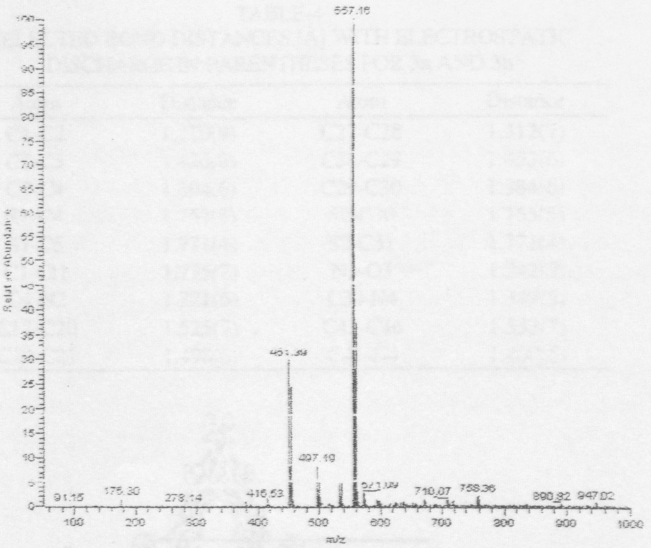


Fig. 4. MS-ESI spectrum of the **3**

Spectroscopic analysis of **3** is found to be in good agreement with the relevant literature. Single yellow crystals of (I) for X-ray analysis were obtained from crystallization by slow evaporation of ethanol.

X-Ray structure determination: Yellow crystals of compound suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanolic solution at room temperature. In compound, $C_{26}H_{23}N_2O_2SCl_3$, having approximate dimensions of 0.50 × 0.40 × 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_α radiation (λ = 0.71070 Å). The data were collected at room temperature to a maximum θ value of 30.2°. Experimental conditions are summarized in Table-2.

TABLE-2
CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE COMPOUND 3

CCDC number	CCDC 738862
Empirical formula	$C_{26}H_{23}N_2O_2SCl_3$
Crystal colour, habit	Yellow, block
Formula weight	533.90
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$ (#33)
Cell dimensions	a = 18.8242(4) Å; b = 9.1910(2)Å; c = 29.4390(6) Å
Volume	5093.3(2) $Å^3$
Z	8
Density (calculated)	1.392 mg/m^3
F_{000}	2208.00
Crystal size	0.5 x 0.4 x 0.2 mm
θ_{limit} (°)	2.2-30.2
Index ranges	$-26 < h < 26$; $-12 < k < 12$; $-41 < l < 41$
Reflections collected	291986
Independent reflections	8287 [$R_{int} = 0.032$]
Data/restraints/parameters	7367/0/659
Goodness of fit indicator	1.163
Final R indices [I>3σ(I)]	$R_1 = 0.086$, $wR_2 = 0.069$
Largest diff. peak and hole	0.80 and -0.45 $e.Å^{-3}$

The structure was solved by SIR92[6] and refined with crystals[7]. 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 $U_{iso}(H) = 1.2U_{eq}(C)$. Final atomic coordinates and equivalent isotropic thermal parameters were listed in Table-3 for 3.

TABLE- 3
FINAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom	x	Y	z	$U_{(eq)}$
Cl1	-0.5771(3)	0.6592(2)	0.9117(6)	0.0825(4)
Cl2	-0.6767(2)	0.7922(2)	0.9714(8)	0.1041(6)
Cl3	-0.7507(8)	0.5058(3)	0.9949(7)	0.0922(5)
S1	-0.5633(6)	0.3371(2)	1.0086(5)	0.0632(3)
O1	-0.7505(2)	0.3731(6)	0.8952(2)	0.101(2)
O2	-0.7020(2)	0.1638(5)	0.9085(2)	0.085(1)
N1	-0.7038(3)	0.2962(6)	0.9126(2)	0.070(1)
N2	-0.5555(2)	0.1268(4)	0.9280(1)	0.0524(8)
C1	-0.6487(4)	0.6262(7)	0.9481(2)	0.087(2)
C2	-0.6743(4)	0.5071(6)	0.9562(3)	0.091(2)
C3	-0.6511(3)	0.3655(5)	0.9398(2)	0.0603(12)
C4	-0.5904(2)	0.2907(5)	0.9536(2)	0.0551(12)
C5	-0.4899(2)	0.3519(5)	1.0088(2)	0.0520(10)
C6	-0.4269(3)	0.3917(5)	0.9738(2)	0.0615(12)
C7	-0.3560(3)	0.3093(6)	0.9787(2)	0.068(1)
C8	-0.3222(2)	0.3581(5)	1.0195(2)	0.0552(11)
C9	-0.2481(3)	0.3750(6)	1.0272(2)	0.073(2)
C10	-0.2188(3)	0.3343(7)	1.0667(2)	0.080(2)
C11	-0.2611(6)	0.2736(10)	1.1011(4)	0.106(3)
C12	-0.3310(4)	0.2535(6)	1.0976(3)	0.087(2)
C13	-0.3638(3)	0.2954(6)	1.0546(2)	0.0556(11)
C14	-0.4391(3)	0.2801(6)	1.0480(2)	0.0548(12)
C15	-0.5625(2)	0.1967(5)	0.8782(2)	0.0549(12)
C16	-0.4925(2)	0.1590(5)	0.8558(2)	0.0556(11)
C17	-0.4671(2)	0.0090(4)	0.8721(2)	0.0516(10)
C18	-0.4556(3)	0.0172(5)	0.9224(2)	0.0619(12)
C19	-0.5226(2)	0.0626(4)	0.9471(2)	0.0573(11)
C20	-0.4011(3)	-0.0405(5)	0.8464(2)	0.0611(13)
C21	-0.3833(2)	-0.1985(5)	0.8516(2)	0.0541(11)
C22	-0.4261(3)	-0.3034(6)	0.8315(2)	0.076(2)
C23	-0.4090(4)	-0.4513(7)	0.8361(2)	0.079(2)
C24	-0.3500(3)	-0.4926(6)	0.8588(2)	0.071(2)
C25	-0.3087(3)	-0.3912(6)	0.8791(2)	0.069(1)
C26	-0.3249(4)	-0.2422(6)	0.8762(3)	0.073(2)

Drawing were performed with the program ORTEP-III[8] with 30 % probability displacement elipsoide in Fig. 5.

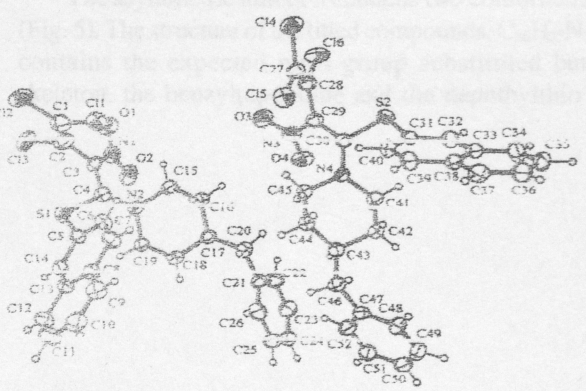


Fig. 5. Asymmetric unit of (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level

The selected bond distances were listed in Table-4. The selected bond and torsion angles were given in Table-5. The packing diagram of compound was given in Fig. 6.

TABLE-4
SELECTED BOND DISTANCES [Å] WITH ELECTROSTATIC DISCHARGE IN PARENTHESES FOR 3a AND 3b

Atom	Distance	Atom	Distance
C1-C2	1.220(9)	C27-C28	1.312(7)
C2-C3	1.456(8)	C28-C29	1.453(6)
C3-C4	1.394(6)	C29-C30	1.384(6)
S1-C4	1.752(5)	S2-C30	1.755(5)
S1-C5	1.771(4)	S2-C31	1.771(4)
C1-Cl1	1.735(7)	N3-O3	1.242(7)
C4-N2	1.321(6)	C30-N4	1.349(5)
C17-C20	1.525(7)	C43-C46	1.533(7)
C20-C21	1.498(6)	C41-N4	1.480(5)

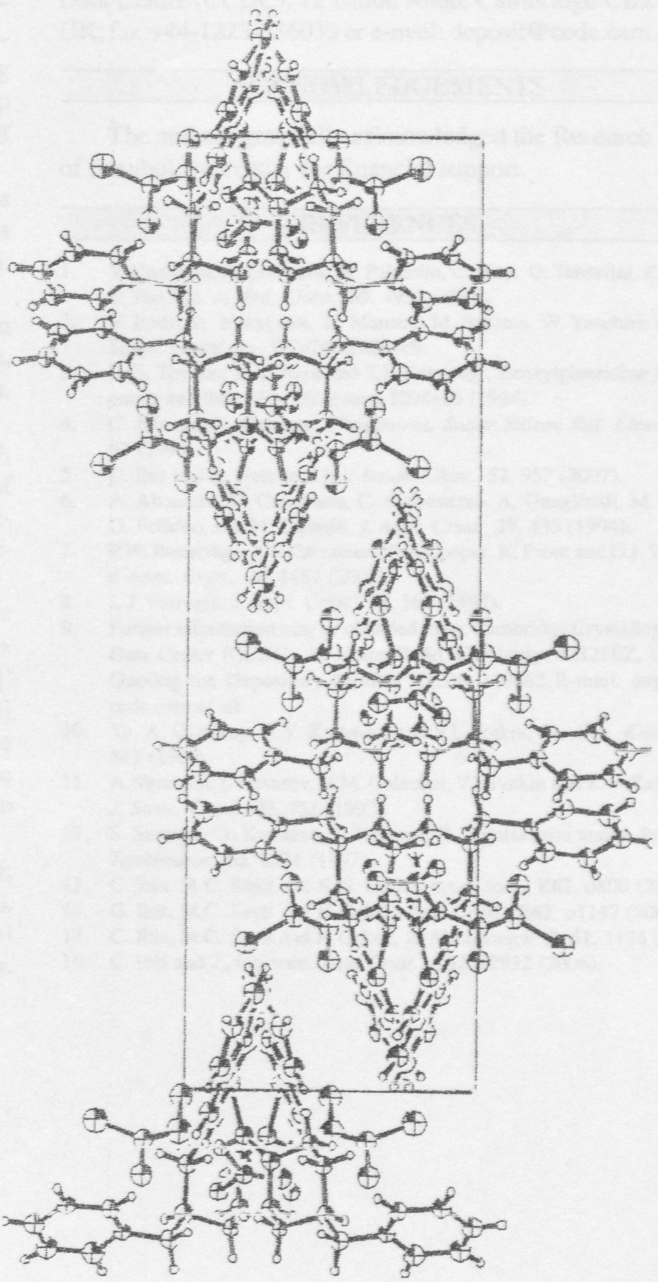


Fig. 6. A view of the crystal packing along with the a axis for the unit cell of 3

TABLE-5
SELECTED BOND AND TORSION ANGLES (°) WITH ELECTROSTATIC DISCHARGE IN PARENTHESES FOR **3a** AND **3b**

Atom	Angle	Atom	Angle
C1-C2-C3	128.2(7)	C1-C2-C3-C4	72.0(1)
C2-C3-C4	126.2(5)	C2-C3-C4-S1	26.3(6)
C6-C5-S1	123.5(3)	N2-C15-C16-C17	58.4(5)
C3-C4-N2	124.3(5)	N2-C19-C18-C17	-51.8(5)
C27-C28-C29	123.7(4)	C27-C28-C29-C30	-66.6(7)
C28-C29-C30	125.3(4)	C28-C29-C30-S2	-30.8(6)

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-738862[9].

RESULTS AND DISCUSSION

The substitution reaction proceeds by an addition-elimination mechanism[10]. First, an addition of the attacking reagent to the C,C double bonds occurs and in a second step the intermediate product is stabilized by elimination of hydrogen chloride.

The compound **3** was obtained in high yield as air stable yellow block-like crystals from the ethanol solution. It is soluble in chloroform, dichloromethane, ethanol, methanol, dioxane, DMSO and DMF, insoluble in water.

In this work, ultraviolet absorption spectra have been recorded in the region 190-900 nm in four solvents (chloroform, methanol, DMF and DMSO). In aprotic and aprotic solvents, two absorption bands appeared at 220-390 nm (Fig. 3).

^{13}C NMR shift of the compound **3**, the signals at δ 126.7, 131.8, 108.8, 155.4 are characteristic of the carbon atoms of the butadiene. In the signals at δ 47.8 (N-CH_2-), 41.3 (aliphatic-CH_2-), 36.7 (CH_2-CH-), 29.9 (CH_2-CH-) are characteristic of the carbon atoms of the piperidine ring.

The ESI mass spectrum of the compound **3** the respective molecular ion peak is observed at m/z (%) 557 [M + 23] + (100). It is likely that this corresponds to the sodium $[Na]^+$ ion. Major fragment F_1 of compound **3** at m/z (%) 451 [M-83] + (100) obtained from the molecular ion by the loss of a nitronium $[NO_2]^+$ and chlorine $[Cl]^+$. The cleavage of chlorine ion from the compound **3** of the molecular ion gives rise to fragment F_2 at m/z (%) 497 (72).

The asymmetric unit of 3 contains two conformers **3a**, **3b**; (Fig. 5). The structure of the titled compounds, $C_{26}H_{23}N_2O_2SCl_3$, contains the expected nitro group substituted butadienyl skeleton, the benzylpiperidine and the naphthylthio groups. The butadiene unit is not planar as would be if the two double bonds were fully conjugated.. Torsion angles of butadiene unit (C1-C2-C3-C4) in **3a** and (C27-C28-C29-C30) in **3b** are 72.0(1)°, -66.6(7)°, respectively. The corresponding bond lengths between the non-H atoms of each conformer are similar. The C-C bond lengths of the butadiene chain agree well with corresponding distances in a similar compound[11-16]. The piperidine ring is not planar with maximum deviation 0.2275(1) Å and it adopts a chair conformation. The perpendicular distances of the two chair atoms in the *para* positions (N2 and C17) from the plane of the other four atoms the six-membered piperidine ring are 0.1384(1) Å and -0.2347(1)Å, respectively.

Supplementary material: CCDC-738862 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at http://www.ccdccam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk

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