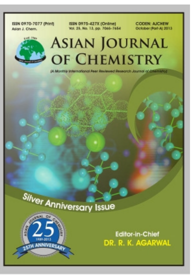
Asian Journal of Chemistry; Vol. 25, No. 14 (2013), 8093-8096

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15136



Synthesis and Crystal Structures of 4,4-Dichloro-2-nitro-1,1,3-*tris*(phenylsulfanyl)-buta-1,3-diene and 4,4-Dichloro-2-nitro-1,1-*bis*(phenylsulfanyl)-3-(phenylsulfinyl)-buta-1,3-diene

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(*Received*: 14 January 2013; *Accepted*: 3 August 2013) AJC-13880

4,4-Dichloro-2-nitro-1,1,3-*tris*(phenylsulfanyl)-buta-1,3-diene **(2)** and dichloro-2-nitro-1,1-*bis*(phenylsulfanyl)-3-(phenylsulfinyl)-buta-1,3-diene **(3)** were synthesized and their crystal structures were determined. The compound **2** is triclinic, space group P-1, a = 9.3328(10), b = 11.6744, c = 11.7894(10) Å, α = 62.460(4), β = 89.639(6), γ = 73.782(5)°, V = 1082.19(2) Å^3, Z = 2. The compound **3** is triclinic, space group P-1, a = 10.9706(7), b = 13.6694(9), c = 15.2581(9) Å, α = 92.470(5), β = 90.204(5), γ = 93.060(6)°, V = 2282.7(2) Å^3, Z = 4. The asymmetric unit of compound **3** contains two crystallographically independent non-planar molecules.

Key Words: Crystal structure, Spectroscopy, Thiosubstituted nitrodiene, X-Ray diffraction.

INTRODUCTION

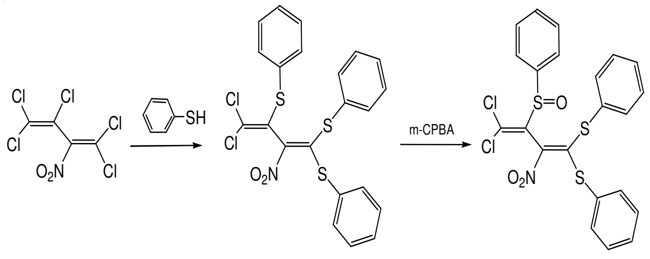
Nitro-substituted polyhalogeno-1,3-butadienes possess valuable synthetic precursors for a variety of polyfunctionalized bioactive compounds[1]. According to a US patent, some thio-substituted dienes also exhibit high biological activity such as insecticide, herbicide and fungicide[2].

In recent years, certain mono-, di-, *tris*(thio) substituted compounds were obtained from the reactions of nitrodienes with thiols and dithiols[3-9]. There are some reports on the crystal structure of these compounds[10-16]. The oxidation reaction of organo sulphur compounds has been the focus of great interest recently in biochemistry and in industrial processes[17]. The reason for this is, partly due to the broad spectrum of biological properties of these compounds.

Previous studies indicate that, sulfone and sulfoxide compounds are formed in the oxidation reaction of some thio ethers with diene groups[18-21] however this is the first study on crystal structure of sulfinyl-nitrobutadiene derivatives.

Halogen derivatives of nitrobutadienes are suitable model objects for elucidating the features of nucleophilic vinylic substitution (S_NVin)[22]. It is well known that in perhalo-2-nitro-buta-1,3-dienes, C-3 and especially C-1 position possesses profound electrophilic character because of the electron-withdrawing property of nitro group. This property allows regioselective substitution of one or two terminal vinylic chlorine substituents (C-1 position) in the nitro dichloro vinyl moiety of the dienes firstly. Third substitution of chlorine atom occurs at the C-3 position[16].

We previously reported the synthesis of the 4,4-dichloro-2-nitro-1,1,3-tris(phenylsulfanyl)-buta-1,3-diene **(2)** and 3,4-dichloro-2-nitro-4-(phenylsulfonyl)-*bis*(phenylsulfanyl)-1,3-butadiene compound[23,24]. The goal of the presented work is to continue the study on this subject by synthesizing to 4,4-dichloro-2-nitro-1,1,3-tris(phenylsulfanyl)-buta-1,3-diene (**2**)[23] for precursor and new dichloro-2-nitro-1,1-*bis*-(phenylsulfanyl)-3-(phenylsulfinyl)-buta-1,3-diene compound (**3**). It is noted that our spectroscopic data are in accordance with the current literature and indicated that compound **2** is not a 1,1,4-substituted, but a 1,1,3-substituted regioisomer instead (**Scheme-I**). New dichloro-2-nitro-1,1-*bis*(phenylsulfanyl)-3-(phenylsulfinyl)-buta-1,3-diene compound (**3**) was obtained by oxidation of **2** and a deep insight into the structural aspect in the solid states, crystallographic analyses of compounds **2** and **3** were conducted and the results are presented in this paper.



1 2 3

Scheme-I

EXPERIMENTAL

Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 elemental analyzer. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometer. NMR spectra were recorded on a Varian UNITY INOVA instrument operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C APT. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS spectrometer according to ESI probe.

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).

General procedure of synthesis 2 and 3: The compound **2** was synthesized from 2-nitro-pentachlorobutadiene **1** and phenyl thiol according to the procedure as reported in the literature and confirmed by comparing the results of melting point, elemental analysis and IR spectroscopy with published data[23]. Yellow crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol at room temperature.

The new compound **3**, was synthesized from a solution containing 4,4-dichloro-2-nitro-1,1,3-*tris*(phenylsulfanyl)-buta-1,3-dien **(2)** (0.2 g, 0.40 mmol) and 3-chloroperbenzoic acid (*m*-CPBA) (0.0045 g, 0.40 mmol) and 30 mL $CHCl_3$ were heated under reflux for 1 h. After completion of the reaction, chloroform was added to the mixture and washed with 2 N $NaHCO_3$ and water (4 mL × 30 mL). The organic layer was separated and dried with Na_2SO_4. The mixture was purified by column chromatography with petroleumether/$CHCl_3$ 1:2 as eluent. Suitable yellow crystals of **3** were obtained by slow evaporation from an ethanol at room temperature.

Yield 61 %, m.p. 149-150.5 ºC. IR (KBr, ν_{max}, cm^{-1}): 3061 (C-H), 1594, 1578 (C=C), 1518, 1289 (NO_2), 1060 (SO). ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 6.90-7.76 (m, 15H, Ar-H). ^{13}C NMR (125.68 MHz, $CDCl_3$): δ = 127.02, 127.54, 128.21, 130.25, 133.44(CH_{arom}), 131.26 (C_{arom}), 129.60, 139.21, 140.11, 162.37 (C_{butad}). $C_{22}H_{15}Cl_2NO_3S_3$ (508.45): calcd. (%) C 51.97, H 2.97, N 2.75, S; found (%) C 52.18, H 3.73, N 3.07. Mass spectra, (ESI$^+$) m/z 508.3 (100 %) (M$^+$).

X-Ray structure determination of 2 and 3: Data collections were carried out on a Rigaku R-Axis Rapid-S diffractometer with graphite monochromatized MoK_α radiation (λ = 0.7109 Å). Experimental conditions are summarized in Table-1. The structures were solved by SIR 92[24] and refined with Crystals[25]. 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

TABLE-1
CRYSTALLOGRAPHIC DATA, EXPERIMENTAL DETAILS AND PARAMETERS OF THE STRUCTURE SOLUTION AND REFINEMENT FOR COMPOUNDS **2** AND **3**

Parameter	Compound **2**	Compound **3**
Chemical formula	$C_{22}H_{15}NO_2S_3Cl_2$	$C_{22}H_{15}NO_3S_3Cl_2$
Molecular weight	492.45	508.45
Crystal system, space group, Z	Triclinic, P-1, 2	Triclinic, P-1, 4
a (Å)	9.3328(10)	10.9706(7)
b (Å)	11.6744	13.6694(9)
c (Å)	11.7894(10)	15.2581(9)
α (º)	62.460(4)	92.470(5)
β (º)	89.639(6)	90.204(5)
γ (º)	73.782(5)	93.060(6)
V (Å^3)	1082.19(2)	2282.7(2)
D_x (g/cm^3)	1.511	1.479
Radiation; λ (Å)	MoK_α, 0.71070	MoK_α, 0.71070
µ (cm^{-1})	6.09	5.83
Temperature T (K)	293	293
Crystal size (mm)	0.60 × 0.40 × 0.20	0.60 × 0.40 × 0.20
Diffractometer	Rigaku R-AXIS RAPID-S	Rigaku R-AXIS RAPID-S
Scan mode Absorption correction; $T_{min,}$ T_{max}	ω/2θ, 0.7614, 1.0000	ω/2θ, 0.731, 0.890
θ_{max} (º)	30.15	30.0
Limiting indices	$-13 \Leftarrow h \Leftarrow 13, -16 \Leftarrow k \Leftarrow 16, -16 \Leftarrow l \Leftarrow 16$	$-15 \Leftarrow h \Leftarrow 15, -19 \Leftarrow k \Leftarrow 17, -21 \Leftarrow l \Leftarrow 21$
Number of reflections measured/number of unique reflactions (N_1), R_{int}/with I > 2σ (I)(N_2)	86064/6352, 0.033/6150	166530/13385, 0.050/10198
Refinment methot	Least-squares prosedure on F^2	Least-squares prosedure on F^2
Number of refined parameters	286	589
Weighting scheme	Chebychev polynomial with 3 parameters (Carruthers & Watkin, 1979) 5.4161, -2.6493, 3.8045	Chebychev polynomial with 3 parameters (Carruthers & Watkin, 1979) 10.4653, -1.4208, 7.9693
Reliability factors: wR_2 relative to N_1 R_1 relative to N_2	0.037, 0.065	0.092, 0.1140
S	1.053	1.118
$\Delta\rho_{min}/\Delta\rho_{max}$, electron (Å^3)	0.46/-0.53	1.20/-0.64
Program package	SIR 92[24], Crystals[25]	SIR 92[24], Crystals[25]

performed using a crystallographic software package[26]. Selected bond distances and bond angles for **2** and **3** are listed in Table-2. ORTEP-III views of the molecular structure of **2** and **3** are given in Figs. 1, 2 and crystal packing diagrams in Figs. 3 and 4[27].

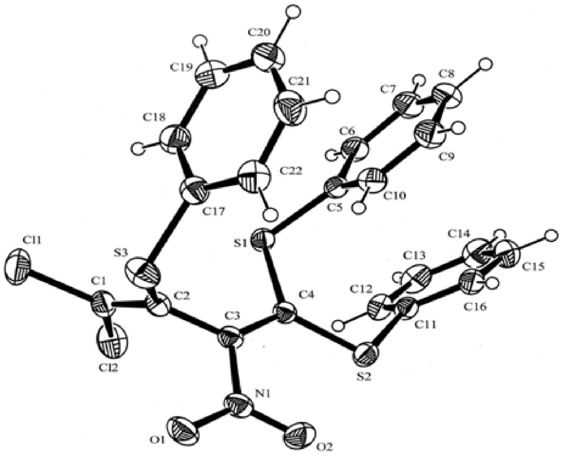


Fig. 1. Molecular structure of compound **2**. Displacement ellipsoids are plotted at the 30 % probability level

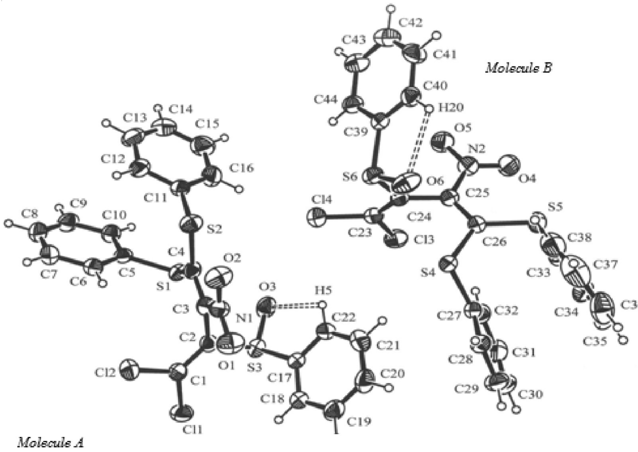


Fig. 2. Molecular structure of compound **3**. Displacement ellipsoids are plotted at the 30 % probability level

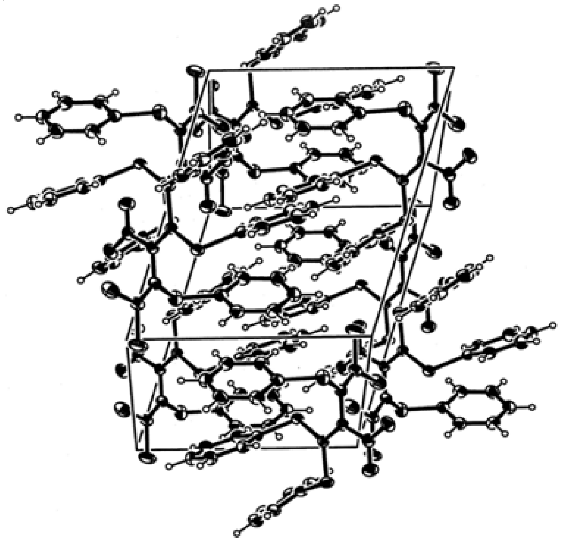


Fig. 3. Unit cell packing diagram for compound **2**; molecular overlap view from the c-axis. The 30 % ellipsoide excluding H atoms

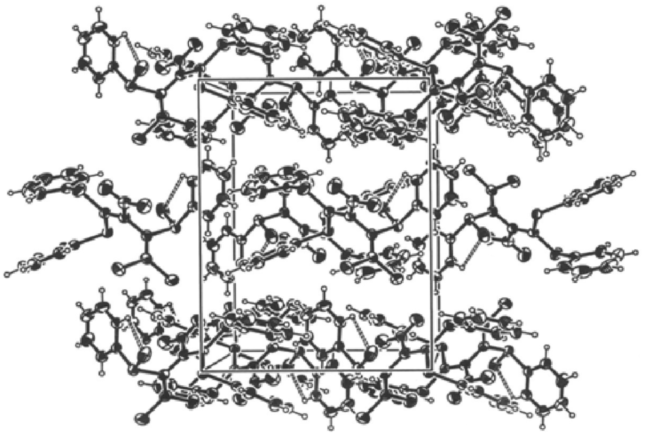


Fig. 4. Unit cell packing diagram for compound **3**; molecular overlap view from the c-axis. 30 % ellipsoide excluding H atoms

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of new compound **3** multiplets that occurred between δ_H 6.90-7.96 could be also distinguished, which were attributed to aromatic protons. In the APT spectrum, the hydrogen atoms bonded aromatic carbons are appeared at the 127.02, 127.54, 128.21, 130.25 and 133.44 ppm values. Four carbon atom signals of the butadiene unit are observed as expected at 129.60, 139.21, 140.11 and 162.37 ppm. The IR spectrum of compound **3** exhibited characteristic absorption peaks at ν = 1060 cm^{-1} corresponding to S=O group, respectively.

The asymmetric unit of **3** contains two independent conformers (A and B, Fig. 2). The corresponding bond lengths between the non-H atoms of each conformer are similar, with differences less than 3 s.u. In both conformers, S=O bond distances were found to be similar to the reference value of 1.471 and 1.479 Å, respectively[28]. The C-C bond lengths of the butadiene chain agree well with corresponding distances in a similar compound[29]. In two molecules, the butadiene unit has assumed a configuration close to *cisoid*, but is not completely planar as it would be if the two double bonds were fully conjugated. Torsion angles of C(4)-C(3)-C(2)-C(1) and C(26)-C(25)-C(24)-C(23) are -98.5(5) and -98.1(5)° for conformer A and B in **3**, the C-C bond lengths of the butadiene unit are 1.365(5), 1.467(5) and 1.327(5) Å, respectively, for C(3)-C(4), C(3)-C(2) and C(2)-C(1) in molecule A. 1.347(5), 1.472(5) and 1.325(5) Å, respectively, for C(25)-C(26), C(25)-C(24) and C(24)-C(23) in molecule B for **3**. In molecule A, dihedral angles formed by the least-squares planes of the phenyl ring connected sulfoxide group and the other two thiophenyl rings being equal to 62.313 and 63.199°. The dihedral angle between the thiophenyl rings is 17.928°. In molecule B, dihedral angles are 60.125, 60.060, 18.274°, respectively. The dihedral differences between molecules A and B are 2.2, 3.1 and 0.3°. The O-S-C-C torsion angles, which are the less worthy differences in bond geometry between A and B, namely, 143.5(3)°[O(3)-S(3)-C(2)-C(1)] *versus* 143.8(3)°[O(6)-S(6)-C(24)-C(23)] for a difference of 0.3°. The close values in the bond lengths, torsion angle and dihedral angles above can be attributed to same conformations of the two molecules.

Intramolecular short contacts between an *ortho*-hydrogen of the phenyl ring and the oxygen of the sulfinyl group are

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

$C_{22}H_{15}NO_2S_3Cl_2$ (**2**)	$C_{22}H_{15}NO_3S_3Cl_2$ (**3**)	–
Bond Dist. Å	Bond Dist. Å	Bond Dist. Å
C(2)-C(1) 1.329(3)	C(2)-C(1) 1.327(5)	C(24)-C(23) 1.325(5)
C(3)-C(2) 1.479(3)	C(2)-C(3) 1.467(5)	C(25)-C(24) 1.472(5)
C(3)-C(4) 1.365(3)	C(4)-C(3) 1.365(5)	C(25)-C(26) 1.347(5)
C(2)-S(3) 1.770(2)	S(3)-O(3) 1.479(3)	S(6)-O(6) 1.471(4)
Angle (°)	Angle (°)	Angle (°)
O(1)-N(1)-O(2) 122.9(1)	O(1)-N(1)-O(2) 122.9(3)	O(5)-N(2)-O(4) 123.5(4)
Cl(2)-C(1)-Cl(1) 112.8(1)	Cl(2)-C(1)-Cl(1) 114.3(2)	Cl(3)-C(23)-Cl(4) 114.4(2)
S(1)-C(4)-S(2) 121.8(1)	S(1)-C(4)-S(2) 120.2(2)	S(4)-C(26)-S(5) 120.2(2)
C(22)-C(17)-S(3) 118.0(1)	C(22)-C(17)-S(3) 117.6(3)	C(40)-C(39)-S(6) 117.5(3)
C(3)-C(2)-S(3) 117.2(1)	C(3)-C(2)-S(3) 116.3(2)	S(6)-C(24)-C(25) 116.4(3)
	O(3)-S(3)-C(2) 105.0(2)	O(6)-S(6)-C(39) 105.6(2)

determined. These attractive interactions have distances less than the sum of O···H van der Waals radii of 2.72 and maintain the sulfinyl and phenyl groups roughly in the same plane. In Table-3, torsion angles around S-C_{Ar} bonds and O···H intramolecular interaction distances are reported.

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°) IN **3**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠DHA
C(22)-H(5)···O(3)	0.950(5)	2.409(5)	2.851(5)	108.1(3)
C(40)H(20)···O(6)	0.950(5)	2.402(6)	2.838(5)	107.7(4)

Torsion angle of C(4)-C(3)-C(2)-C(1) is 79.4(2)° for **2**. The C-C bond lengths of the butadiene unit are 1.365(3), 1.479(3) and 1.329(3) Å, respectively, for C(3)-C(4), C(3)-C(2) and C(2)-C(1) in **2**. The three phenyl rings are inclined with the butadiene group at angles of 18.4(1), 30.3(1) and 46.3(1)° for **2**. The average bond length of C-S, not oxidized to sulfoxide, is 1.763(2) and 1.762(4) Å, respectively in **2** and **3**. This average bond length is considerably shorter compared to the corresponding bond lengths of C(2)-S(3) and C(24)-S(6), oxidized to sulfoxide, in **3** (1.827 (4) Å). This may be explained by intramolecular hydrogen bond in **3**. Differences of the torsion angles of butadiene moiety and dihedral angles of phenyl rings in both compounds are attributed to the same reason.

Supplementary material

Crystallographic data for the compound **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 893383 and CCDC 720157. Copies of available material can be obtained, free of charge, by application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk; Fax: +44-(0)1223-336033).

ACKNOWLEDGEMENTS

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

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