Russian Journal of General Chemistry, Vol. 72, No. 12, 2002, pp. 1927–1933. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 12, 2002, pp. 2035–2041.
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Synthesis and Structure of Dinitrosulfodienes of the Thiolene 1,1-Dioxide Series

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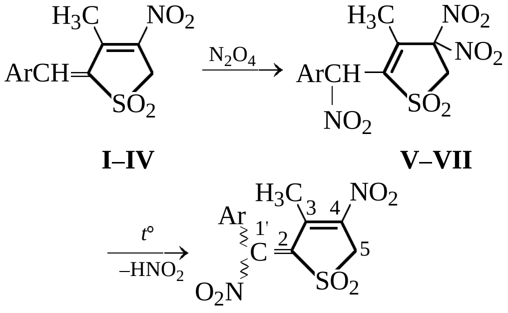
Received September 21, 2001

Abstract—A synthesis of previously unknown rigidly fixed heterocyclic structures, dinitrosulfodienes of the thiolene 1,1-dioxide series, was developed, and their structure was studied. The geometry and structural parameters of 3-methyl-4-nitro-2-[nitro(phenyl)methylene]-3-thiolene 1,1-dioxide were determined by X-ray diffraction.

Activated diene systems are widely used in organic synthesis for preparing diverse functionally-substituted organic compounds. In particular, 2-benzylidene-3-methyl-4-nitro-3-thiolene 1,1-dioxides proved to be original models for studying specific features of the chemical behavior of a nitrodiene system incorporated into the thiolene dioxide ring, as well as convenient starting materials for syntheses on the basis of nucleophilic substitution reactions [1–4].

To prepare dinitrosulfodienes of the thiolene 1,1-dioxide series, we performed nitration of 2-benzylidene-3-methyl-4-nitro-3-thiolene 1,1-dioxides **I**–**IV** with various substituents in the benzene ring. The reactions occurred in carbon tetrachloride solutions at room temperature; as nitrating agent we used dinitrogen tetroxide. The nitration of compounds **I**–**III** gave 3-methyl-4,4-dinitro-2-[aryl(nitro)methyl]-2-thiolene 1,1-dioxides **V**–**VII** in ~50% yields.



I–**IV** **V**–**VII**

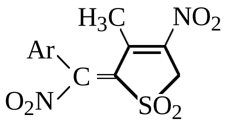
VIIIa, VIIIb–**XIa, XIb**

Ar = C_6H_5 (**I, V, VIIIa, VIIIb**), *p*-MeC_6H_4 (**II, VI, IXa, IXb**), *p*-ClC_6H_4 (**III, VII, Xa, Xb**), *p*-$NO_2C_6H_4$ (**IV, XIa, XIb**).

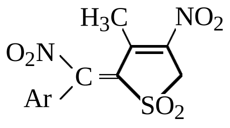
When heated for a short time in polar solvents (methanol, acetone), compounds **V** and **VII** undergo 1,4 elimination of nitrous acid and convert to dinitrosulfodienes **VIII** and **X** in nearly quantitative yields. The necessity in longer heating in the synthesis of compound **IX** is probably associated with the electron-donor nature of the substituent in the benzene ring. By contrast, the NO_2 substituent in the aromatic system of compound **IV** prevents formation of the corresponding trinitro derivative and favors spontaneous elimination of HNO_2 to give dinitrodiene **XI**. The latter is readily obtained by independent synthesis, by nitration of compound **VIII** with fuming nitric acid.

Trinitro derivatives **V**–**VII** are colorless crystalline substances. Their structure was established on the basis of spectral evidence and elemental analysis (Table 1). The ^1H NMR spectra contain singlet signals of the methyl (2.01–2.12 ppm), methylene (4.36–4.70 ppm), nitromethine (6.60–7.04 ppm), and aromatic protons (7.25–7.5 ppm). The IR spectra display absorption bands of the multiple bonds (1610 cm^{-1}) and geminal nitro- (1570–1580, 1390 cm^{-1}) and sulfonyl groups (1340–1345, 1150–1170 cm^{-1}).

Dinitrosulfodienes **VIII**–**XI** are stable yellow crystalline substances. They are formed as mixtures of *Z,E-s-trans* and *E,E-s-trans* isomers. *Z,E* Isomers **VIIIa**, **Xa**, and **XIa** could be isolated pure by fractional crystallization and column chromatography.



Z,E-s-trans



E,E-s-trans

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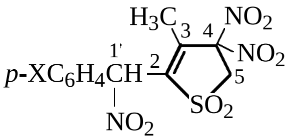
Table 1. Physicochemical and spectral characteristics of 3-methyl-4,4-dinitro-2-[nitro(phenyl)methyl]-2-thiolene 1,1-dioxides **V–VII**



Comp. no.	X	Yield, %	mp, °C	IR spectrum (KBr), ν, cm^{-1}			^{1}H NMR spectrum (CD$_3$CN), δ, ppm			
				C=C	C(NO$_2$)$_2$	SO$_2$	CH$_3$	CH$_2$	CH	Ar
V	H	52	105–106	1610	1570, 1390	1345, 1160	2.06	4.68	7.04	7.48
VI	CH$_3$	24	102–105	1610	1570, 1390	1340, 1150	2.01	4.36	6.60	2.42, 7.25
VII	Cl	50	100–105	1610	1580, 1390	1340, 1170, 1150	2.12	4.70	6.93	7.50

Table 2. Physicochemical and spectral characteristics of 3-methyl-4-nitro-2-[aryl(nitro)methylene]-3-thiolene 1,1-dioxides **VIII–XI**

Comp. no.	Ar	Isomer	Yield, %	mp, °C	IR spectrum (KBr),[a] ν, cm^{-1}			UV spectrum (CHCl$_3$)		^{1}H NMR spectrum (CDCl$_3$), δ, ppm		
					C=C	=CNO$_2$	SO$_2$	λ, nm	ε	CH$_3$	CH$_2$	Ar
VIIIa	C$_6$H$_5$	*Z,E*	92	155–158	1610, 1590	1540, 1510, 1380	1345, 1160, 1140	255 288 343	2700 10000 13000	1.95	4.55	7.30, 7.65
VIIIb		*E,E*[b]				1330				2.45	4.45	7.30, 7.65
IXa	C$_6$H$_4$CH$_3$-*p*	*Z,E*	70	98–102[c]	1610, 1590	1540, 1520, 1340	1340, 1150	250 365	10200 3700	1.98	4.52	2.45, 7.30
IXb		*E,E*[b]								2.40	4.45	2.45, 7.50
Xa	C$_6$H$_4$Cl-*p*	*Z,E*	90	160–162	1610, 1590	1545, 1520, 1340	1310, 1170, 1140	264 278 354	8000 7900 8900	1.90	4.55	7.35, 7.60
Xb		*E,E*[b]								2.40	4.45	7.60
XIa	C$_6$H$_4$NO$_2$-*p*	*Z,E*	97	172–174	1610	1580, 1540	1335, 1165	266 311	11000 12000	1.85	4.55	7.85, 8.45
		E,E[b]				1360	1140			2.50	4.40	8.05

[a] The IR spectra of individual *Z,E* isomers are identical to the spectra of mixtures of the *Z,E* and *E,E* isomers. [b] *E,E* Isomers **VIIIb–XIb** were identified in mixtures with *Z,E* isomers **VIIIa–XIa** by ^{1}H NMR spectroscopy. [c] The melting points and spectral characteristics are given for a mixture of the *Z,E* and *E,E* isomers, 3 : 1 (by ^{1}H NMR).

The structural isomers of compounds **VIII**–**XI** were identified by the methyl proton signals in the ^{1}H NMR spectra ($\Delta\delta_{CH_3}$ ~0.5 ppm) (Table 2). Because of the strong deshielding through-space effect of the nitro groups, the methyl protons of the *E,E* isomers appear downfield (2.40–2.50 ppm) compared with those of the *Z,E* isomers (1.85–1.98 ppm). The methylene protons are less sensitive to differences in the electronic organization of the geometric isomers. At the same time, in the *Z,E* isomers, where the nitro group is proximate to sulfonyl and thus indirectly affects its environment, the methylene protons absorb downfield (4.55 ppm) from those of the *E,E* form (4.40–4.45 ppm). The aromatic proton signals of compounds **VIII**–**XI** are at 7.30–8.45 ppm. The IR spectra of compounds **VIII**–**X** contain absorption

Table 3. Bond lengths *d* in molecule **VIIIa**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
$S^1–O^{11}$	1.439(3)	$C^2–C^6$	1.351(5)	$C^9–C^{10}$	1.388(9)
$S^1–O^{12}$	1.412(4)	$C^3–C^4$	1.361(6)	$C^9–H^9$	0.98(7)
$S^1–C^2$	1.802(4)	$C^3–C^{13}$	1.480(7)	$C^{10}–C^{11}$	1.370(9)
$S^1–C^5$	1.791(5)	$C^4–C^5$	1.478(7)	$C^{10}–H^{10}$	0.95(4)
$O^{41}–N^4$	1.227(7)	$C^5–H^{51}$	0.82(6)	$C^{11}–C^{12}$	1.375(7)
$O^{42}–N^4$	1.230(5)	$C^5–H^{52}$	1.09(3)	$C^{11}–H^{11}$	1.26(9)
$O^{61}–N^6$	1.233(4)	$C^6–C^7$	1.449(6)	$C^{12}–H^{12}$	1.00(6)
$O^{62}–N^6$	1.217(5)	$C^7–C^8$	1.392(7)	$C^{13}–H^{131}$	1.09(4)
$N^4–C^4$	1.458(6)	$C^7–C^{12}$	1.401(7)	$C^{13}–H^{132}$	0.83(5)
$N^6–C^6$	1.489(6)	$C^8–C^9$	1.394(6)	$C^{13}–H^{133}$	1.00(5)
$C^2–C^3$	1.472(6)	$C^8–H^8$	1.09(8)		

bands of the multiple bonds (1610–1590 cm^{-1}), sulfonyl (1345–1310, 1170–1140 cm^{-1}), and conjugated nitro groups (1580–1520, 1380–1340 cm^{-1}) (Table 2). The electronic absorption spectra of dinitrosulfolenes **VIII**–**XI** display absorption bands at λ_{max} 250–350 nm. The much lower band intensity compared with linear 1,4-dinitro-1,3-butadienes (λ_{max} 281 nm, ε 22500) [5, 6] suggests disturbed conjugation in the diene systems studied (Table 2).

A more complete information on the structure of the *Z,E* isomer of 3-methyl-4-nitro-2-[nitro(phenyl)-methylene]-3-thiolene 1,1-dioxide (**VIIIa**) was obtained by X-ray diffraction analysis (Fig. 1). It was found that compound **VIIIa** in crystal has the following structure. The conformation of the five-membered unsaturated heteroring is *envelope* with C^1 deviating from the plane formed by the other four atoms. The nitro group at C^4, too, locates in that plane (the $O^{41}N^4C^4C^3$ torsion angle is –6.5°) inspite of the steric repulsion from the *cis*-methyl substituent, which makes the $N^4–C^4=C^3$ and $Me–C^3=C^4$ bond angles larger by ~6° compared with the $N^4C^4C^5$ and MeC^3C^2 angles. Because of the strong repulsion between the nitro and sulfonyl oxygen atoms, the nitro group at the exocyclic double bond is turned by 50.8°, which much restricts its involvement in conjugation.

The principal geometric parameters of the molecule (bond lengths and bond and torsion angles) are given in Tables 3–5, respectively. In **VIIIa**, there is a short 1,5 nonbonded contact $S^1\cdots O^{62}$ 2.988(3) Å, which is 0.33 Å smaller than the sum of the van der Waals radii of oxygen and sulfur. Shorter nonbonded contacts 1,5-S···O involving a two-coordinate sulfur atom were observed in compounds where the sulfur atom and the nitro group are in the *ortho* position of the benzene ring [7]. In such structures, the S···O distance varies from 2.38 to 2.80 Å, depending on substituent on the sulfur atom; it is minimal in *o*-$ClSC_6H_4NO_2$ and *o*-$MeOSC_6H_4NO_2$ [8] and maximal when the sulfur atom has two neighboring carbon atoms [9–12].

The crystal packing of **VIIIa** is defined by intermolecular interactions, namely, C–H···O hydrogen bonds involving an acceptor (exocyclic nitro group) and donor (methylene hydrogens of the heteroring and the phenyl ring) (Fig. 2) and having the following parameters: $C^5–H^{51}\cdots O^{61b}$ [2 – *x*, –*y*, –*z*], $C^5–H^{51}$ 0.82(6), $H^{51}\cdots O^{61b}$ 2.57(5), $C^5\cdots O^{61b}$ 3.293(6) Å, ∠149(4)°; $C^{10}–H^{10}\cdots O^{61a}$ [1 – *x*, –*y*, 1 – *z*], $C^{10}–H^{10}$ 0.95(4), $H^{10}\cdots O^{61a}$ 2.60(5), $C^{10}\cdots O^{61a}$ 3.410(7) Å, $\angle C^{10}–H^{10}\cdots O^{61a}$ 144(4)°. These contacts form centrosymmetric dimers of molecules **VIIIa**, but, since each molecule forms two H-bonded dimers (via different symmetry centers), the crystal contains an infinite chain of pairs of dinitrosulfodiene molecules (Fig. 2).

Thus, in the present work we developed for the first time methods of synthesis of dinitrosulfodienes of the thiolene 1,1-dioxide series and assessed their structure by means of IR, ^1H NMR, and UV spec-

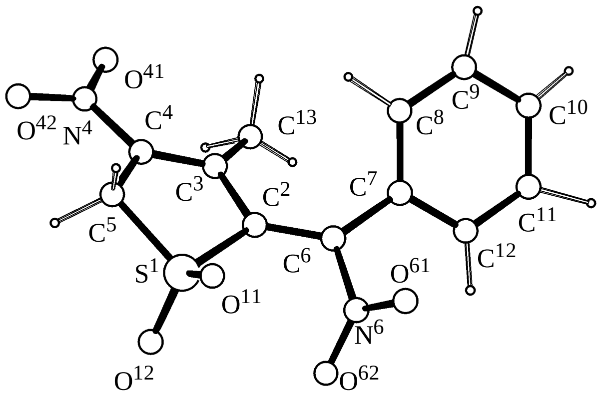


Fig. 1. Geometry of molecule **VIIIa** in crystal.

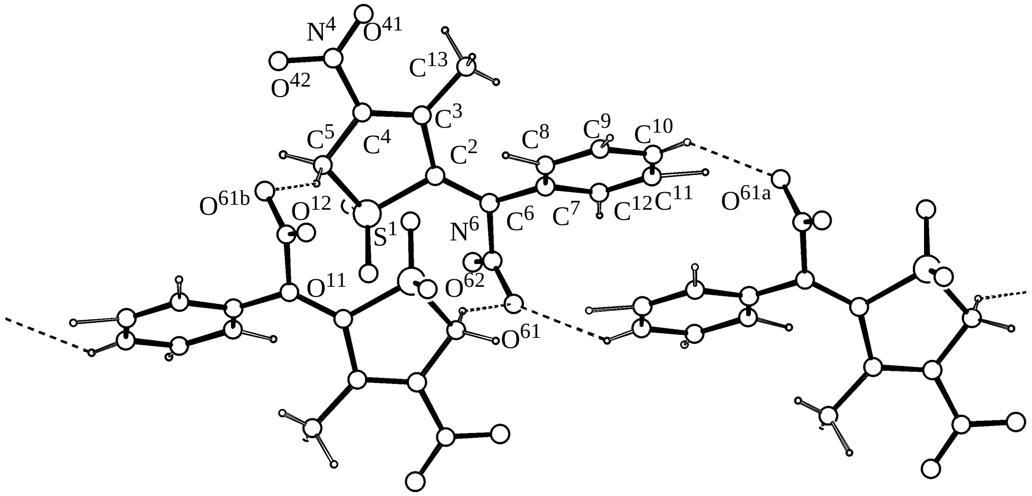


Fig. 2. Hydrogen bonds C–H···O in the crystal of compound **VIIIa** (H bonds are shown by dotted lines).

troscopy. X-ray diffraction was used to determine the molecular geometry, structural parameters, and crystal packing of the *Z,E* isomer of 3-methyl-4-nitro-2-[nitro(phenyl)methylene]-3-thiolene 1,1-dioxide.

EXPERIMENTAL

The IR spectra were measured on Specord IR-75 and UR-20 spectrophotometers on KBr pellets in the frequency ranges of LiF and NaCl prisms.

The electronic absorption spectra were measured on Specord M-40 and SF-46 instruments in quartz cells, solvent chloroform.

The ^{1}H NMR spectra were obtained on a Bruker AC-200 spectrometer (200 MHz) in acetonitrile-d_3 (**V**–**VII**) and chloroform-d_1 (**III, VIII**–**XI**). The chemical shifts were measured in δ against internal or external HMDS with an accuracy of ±0.5 Hz.

2-Benzylidene-3-methyl-4-nitro-3-thiolene-1,1-dioxides **I**, **II**, and **IV** were prepared by known procedures [2].

Table 4. Bond angles ω in molecule **VIIIa**

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O^{11}S^1O^{12}$	118.8(2)	$N^4C^4C^3$	122.8(4)	$C^8C^7C^{12}$	119.7(4)
$O^{11}S^1C^2$	109.2(2)	$N^4C^4C^5$	116.2(4)	$C^7C^8C^9$	119.5(5)
$O^{11}S^1C^5$	111.6(2)	$C^3C^4C^5$	120.9(4)	$C^7C^8H^8$	123.0(3)
$O^{12}S^1C^2$	112.8(2)	$S^1C^5C^4$	103.5(3)	$C^9C^8H^8$	117.0(3)
$O^{12}S^1C^5$	108.7(2)	$C^{12}C^{11}H^{11}$	134.0(4)	$C^8C^9C^{10}$	120.2(6)
$C^2S^1C^5$	92.7(2)	$C^7C^{12}C^{11}$	119.4(5)	$C^8C^9H^9$	131.0(4)
$O^{41}N^4O^{42}$	124.5(4)	$C^7C^{12}H^{12}$	119.0(3)	$C^{10}C^9H^9$	108.0(4)
$O^{41}N^4C^4$	119.7(4)	$C^3C^{13}H^{131}$	105.0(2)	$C^9C^{10}C^{11}$	119.7(5)
$O^{42}N^4C^4$	115.7(4)	$S^1C^5H^{51}$	105.0(4)	$C^9C^{10}H^{10}$	113.0(4)
$O^{61}N^6O^{62}$	123.8(4)	$S^1C^5H^{52}$	106.0(2)	$C^{11}C^{10}H^{10}$	127.0(4)
$O^{61}N^6C^6$	117.3(3)	$C^4C^5H^{51}$	113.0(3)	$C^{10}C^{11}C^{12}$	121.4(5)
$O^{62}N^6C^6$	118.9(3)	$C^4C^5H^{52}$	113.0(2)	$C^{10}C^{11}H^{11}$	105.0(4)
$S^1C^2C^3$	109.4(2)	$H^{51}C^5H^{52}$	115.0(4)	$C^3C^{13}H^{132}$	104.0(3)
$S^1C^2C^6$	122.7(3)	$N^6C^6C^2$	116.0(4)	$C^3C^{13}H^{133}$	105.0(3)
$C^3C^2C^6$	127.7(4)	$N^6C^6C^7$	113.8(3)	$H^{131}C^{13}H^{132}$	117.0(4)
$C^2C^3C^4$	108.9(4)	$C^2C^6C^7$	130.1(4)	$H^{131}C^{13}H^{133}$	112.0(4)
$C^2C^3C^{13}$	122.2(4)	$C^6C^7C^8$	120.4(4)	$H^{132}C^{13}H^{133}$	113.0(4)
$C^4C^3C^{13}$	128.7(4)	$C^6C^7C^{12}$	119.9(4)		

Table 5. Torsion angles τ in molecule **VIIIa**

Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$O^{11}S^{1}C^{2}C^{3}$	–134.0(3)	$O^{42}N^{4}C^{4}C^{5}$	–1.4(6)	$C^{3}C^{2}C^{6}C^{7}$	12.2(8)
$O^{11}S^{1}C^{2}C^{6}$	40.7(4)	$O^{61}N^{6}C^{6}C^{2}$	–128.0(4)	$C^{2}C^{3}C^{4}N^{4}$	–177.3(4)
$O^{12}S^{1}C^{2}C^{3}$	91.6(3)	$O^{61}N^{6}C^{6}C^{7}$	49.6(5)	$C^{2}C^{3}C^{4}C^{5}$	–1.4(6)
$O^{12}S^{1}C^{2}C^{6}$	–93.8(4)	$O^{62}N^{6}C^{6}C^{2}$	50.8(5)	$C^{13}C^{3}C^{4}N^{4}$	–3.3(8)
$C^{5}S^{1}C^{2}C^{3}$	–20.0(3)	$O^{62}N^{6}C^{6}C^{7}$	–131.6(4)	$C^{13}C^{3}C^{4}C^{5}$	172.7(5)
$C^{5}S^{1}C^{2}C^{6}$	154.6(4)	$S^{1}C^{2}C^{3}C^{4}$	15.4(4)	$N^{4}C^{4}C^{5}S^{1}$	163.2(3)
$O^{11}S^{1}C^{5}C^{4}$	129.6(3)	$S^{1}C^{2}C^{3}C^{13}$	–159.1(4)	$C^{3}C^{4}C^{5}S^{1}$	–13.0(5)
$O^{12}S^{1}C^{5}C^{4}$	–97.4(3)	$C^{6}C^{2}C^{3}C^{4}$	–158.9(4)	$N^{6}C^{6}C^{7}C^{8}$	–135.2(4)
$C^{2}S^{1}C^{5}C^{4}$	17.7(3)	$C^{6}C^{2}C^{3}C^{13}$	26.6(7)	$N^{6}C^{6}C^{7}C^{12}$	43.1(6)
$O^{41}N^{4}C^{4}C^{3}$	–6.5(7)	$S^{1}C^{2}C^{6}N^{6}$	15.7(6)	$C^{2}C^{6}C^{7}C^{8}$	41.9(7)
$O^{41}N^{4}C^{4}C^{5}$	177.3(5)	$S^{1}C^{2}C^{6}C^{7}$	–161.5(4)	$C^{2}C^{6}C^{7}C^{12}$	–139.8(5)
$O^{42}N^{4}C^{4}C^{3}$	174.8(5)	$C^{3}C^{2}C^{6}N^{6}$	–170.7(4)		

X-ray diffraction study. Compound **VIIIa** was obtained as yellow triclinic crystals. The unit cell parameters at 20°C are as follows: a 8.287(5), b 8.802(4), c 9.913(4) Å; α 70.15(2), β 78.13 (4), γ 88.80(2)°; V 665(1) Å^3, Z 2, d_{calc} 1.595 g/cm^3, space group P-1. The unit cell parameters and the intensities of 2887 reflections, 1960 of which had $I \geq 3\sigma$, were measured on an Enraf–Nonius CAD-4 automatic four-circle diffractometer at 20°C ($\lambda \text{Cu}K_\alpha$ radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 70°$). No intensity decay of the three control reflections was observed during experiment. Empirical corrections for absorption were applied (μCu 24.17 cm^{-1}).

The structure was solved by the direct method by the SIR program [13] and refined first isotropically and then anisotropically. All hydrogen atoms were revealed by difference synthesis, and included in structure amplitudes with fixed positional and isotropic thermal parameters. The final divergence factors were R 0.067 and R_W 0.076 (on 1542 unique reflections with $F^2 > 3\sigma$). All calculations were performed on an Alpha Station 200 computer using the MolEN program package [14]. The drawings were made and the intermolecular contacts in crystal were analyzed by the PLATON program [15]. The atomic coordinates are listed in Table 6.

2-(*p*-Chlorobenzylidene)-3-methyl-4-nitro-3-thiolene 1,1-dioxide (III) was obtained similarly to compound **I** [2]. Yield 30%, mp 194–195°C (from ethanol). Found, %: C 48.13, 48.09; H 3.48, 3.45; N 4.70, 4.71. $C_{12}H_{10}ClNO_4S$. Calculated, %: C 48.08; H 3.34; N 4.67.

3-Methyl-4,4-dinitro-2-[nitro(phenyl)methyl]-2-thiolene 1,1-dioxide (V). Dinitrogen tetroxide, 4 ml, was added dropwise with stirring at room temperature to a suspension of 1 g of 2-benzylidene-3-methyl-4-

Table 6. Atomic coordinates in structure **VIIIa**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j)B(i,j)$ (Å^2) and isotropic thermal parameters of hydrogen atoms B_{iso} (Å^2)

Atom	x	y	z	B
S^{1}	1.1125(1)	0.2597(1)	0.9130(1)	2.60(2)
O^{11}	1.1701(4)	0.1110(4)	1.0009(3)	4.00(8)
O^{12}	1.2090(4)	0.4045(4)	0.8737(4)	3.90(8)
O^{41}	0.7010(6)	0.3946(6)	0.6085(4)	7.3(1)
O^{42}	0.9411(6)	0.3327(5)	0.5099(3)	6.6(1)
O^{61}	0.9581(4)	0.0865(4)	1.3334(3)	3.99(8)
O^{62}	1.0722(4)	0.3216(4)	1.1962(3)	3.64(7)
N^{4}	0.8409(6)	0.3483(5)	0.6140(4)	4.2(1)
N^{6}	0.9663(4)	0.2140(4)	1.2291(3)	2.54(7)
C^{2}	0.8993(5)	0.2765(4)	0.9914(4)	2.18(8)
C^{3}	0.8049(6)	0.3264(5)	0.8742(4)	2.55(9)
C^{4}	0.8962(6)	0.3041(5)	0.7522(4)	2.98(9)
C^{5}	1.0637(7)	0.2426(6)	0.7508(4)	3.7(1)
C^{6}	0.8405(5)	0.2341(5)	1.1375(4)	2.60(9)
C^{7}	0.6722(6)	0.1979(5)	1.2217(4)	2.79(9)
C^{8}	0.5631(6)	0.1046(6)	1.1886(5)	3.5(1)
C^{9}	0.4013(6)	0.0728(7)	1.2696(6)	4.6(1)
C^{10}	0.3505(7)	0.1305(8)	1.3849(6)	5.0(1)
C^{11}	0.4601(7)	0.2195(7)	1.4181(5)	4.2(1)
C^{12}	0.6203(6)	0.2534(6)	1.3396(4)	3.3(1)
C^{13}	0.6446(6)	0.4026(6)	0.8917(5)	3.5(1)
H^{8}	0.592(7)	0.067(9)	1.092(8)	11(2)
H^{9}	0.312(8)	–0.000(8)	1.270(7)	10(2)
H^{10}	0.238(5)	0.102(6)	1.432(5)	5(1)
H^{11}	0.376(9)	0.26(1)	1.519(9)	15(3)
H^{12}	0.704(6)	0.302(7)	1.375(6)	6(1)
H^{51}	1.066(6)	0.146(6)	0.764(5)	6(1)
H^{52}	1.158(4)	0.319(5)	0.659(4)	2.6(9)
H^{131}	0.661(6)	0.515(6)	0.798(5)	5(1)
H^{132}	0.631(5)	0.411(6)	0.974(5)	5(1)
H^{133}	0.562(5)	0.325(5)	0.886(4)	3(1)

nitro-3-thiolene 1,1-dioxide (**I**) in 15 ml of carbon tetrachloride. Compound **I** gradually dissolved. The reaction mixture was left to stand for 40 min. After removal of the solvent and excess N_2O_4, a white precipitate formed and was washed with diethyl ether to obtain 0.68 g (52%) of compound **V**, mp 105–106°C (decomp.). Found, %: C 40.57, 40.58; H 3.34, 3.33; N 11.92, 11.91. $C_{12}H_{12}N_3O_8S$. Calculated, %: C 40.34; H 3.08; N 11.76.

3-Methyl-4,4-dinitro-2-[nitro(*p*-tolyl)methyl]-2-thiolene 1,1-dioxide (VI) was obtained in a similar way from compound **II**. Yield 24%, mp 102–105°C (decomp.). Found, %: C 42.12, 42.10; H 3.63, 3.63; N 11.31, 11.30. $C_{13}H_{13}N_3O_8S$. Calculated, %: C 42.05; H 3.50; N 11.32.

2-[(*p*-Chlorophenyl)nitromethyl]-3-methyl-4,4-dinitro-2-thiolene 1,1-dioxide (VII) was obtained in a similar way from compound **III**, except that the reaction mixture was left to stand for 60 min. Yield 50%, mp 100–105°C (decomp.). Found, %: C 36.78, 36.80; H 2.53, 2.60; N 10.72, 10.77. $C_{12}H_{10}ClN_3O_8S$. Calculated, %: C 36.78; H 2.55; N 10.77.

3-Methyl-4-nitro-2-[nitro(phenyl)methylene]-3-thiolene 1,1-dioxide (VIII). A suspendion of 0.3 g of compound **V** in 3 ml of methanol was heated for 1–2 min on a sand bath. Nitrogen oxides evolved, the starting compound dissolved, and yellow crystals formed. The mixture was cooled to room temperature and filtered to obtain 0.24 g (92%) of compound **VIII** as a 3 : 2 *Z*,*E*: *E*,*E* mixture (by ^{1}H NMR), mp 130–135°C (from methanol). Found, %: C 46.74, 46.73; H 3.37, 3.45; N 9.05, 9.08. $C_{12}H_{10}N_2O_6S$. Calculated, %: C 46.45; H 3.23; N 9.03.

The mixture was separated by column chromatography (eluent benzene) or fractional crystallization from benzene to obtain individual *Z,E* isomer **VIIIa**, mp 155–158°C (from benzene).

3-Methyl-4-nitro-2-[nitro(*p*-tolyl)methylene]-3-thiolene 1,1-dioxide (IX) was obtained from compound **VI** similarly to compound **VIII**, except that the reaction mixture was left to stand for 20 min. A mixture of *Z*,*E* and *E*,*E* isomers **IXa** and **IXb** (3 : 1, by ^{1}H NMR) was isolated, yield 70%, mp 98–102°C (from methanol). Found N, %: 8.35, 8.32. $C_{13}N_{12}H_2 \cdot O_6S$. Calculated N, %: 8.64.

2-[(*p*-Chlorophenyl)nitromethylene]-3-methyl-4-nitro-3-thiolene 1,1-dioxide (X) was obtained from compound **VII** similarly to compound **VIII**. A mixture of *Z*,*E* and *E*,*E* isomers **Xa** and **Xb** (3 : 2, by ^{1}H NMR) was isolated, yield 90%, mp 135–138°C (from methanol). Found, %: C 41.74, 41.75; H 2.78, 2.78; N 8.26, 8.24. $C_{12}H_9ClN_2O_6S$. Calculated, %: C 41.80; H 2.61; N 8.13.

The mixture was separated by fractional crystallization from benzene to obtain individual *Z,E* isomer **Xa**, mp 160–162°C (from benzene).

3-Methyl-4-nitro-2-[nitro(*p*-nitrophenyl)methylene]-3-thiolene 1,1-dioxide (XI). *a*. Dinitrogen tetroxide, 6 ml, was added dropwise with stirring at room temperature to a suspension of 0.3 g of compound **IV** in 15 ml of carbon tetrachloride. The reaction mixture was left to stand for 90 min, and the solvent was evaporated to leave an oily substance which was crystallized with methanol. A mixture of *Z*,*E* and *E*,*E* isomers **XIa** and **XIb** (2 : 3, by ^{1}H NMR) was obtained, yield 0.4 g (35%), mp 169–170°C (from methanol). Found, %: C 40.65, 40.67; H 2.62, 2.64; N 11.88, 11.90. $C_{12}H_9N_3O_8S$. Calculated, %: C 40.56; H 2.50; N 11.80.

b. Fuming nitric acid, 1 ml, was added dropwise with stirring at 0°C to a suspension of 0.3 g of compound **VIIIa** in 10 ml of carbon tetrachloride. The mixture was left to stand for 15 min and poured into ice water to isolate 0.3 g (97%) of *Z,E* isomer **XIa** as yellow crystals, mp 172–174°C (from acetone–chloroform, 1 : 1). Found, %: C 41.37, 41.37; H 2.37, 2.35; N 11.98, 11.92. $C_{12}H_9N_3O_8S$. Calculated, %: C 40.56; H 2.50; N 11.80.

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