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Halo Derivatives of 2,4-Dinitrothiolene 1,1-Dioxides: Synthesis and Structure

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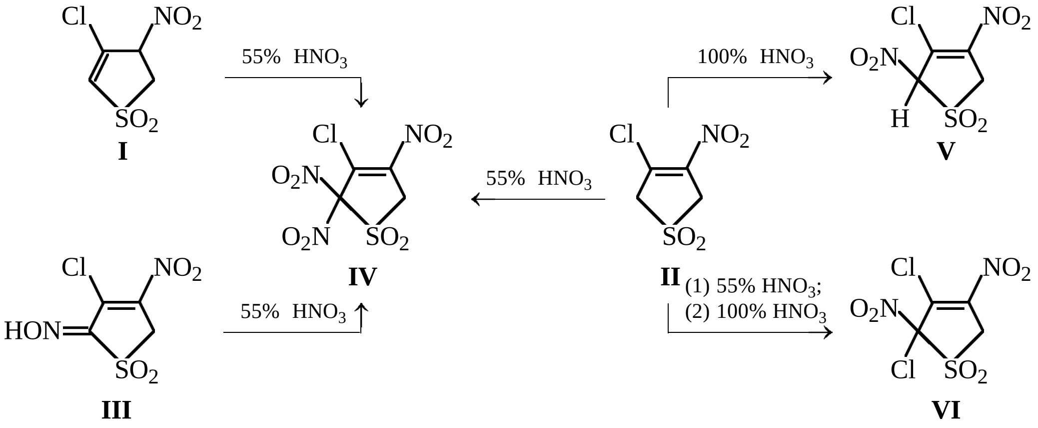
Abstract—Procedures were developed for preparing representatives of a new type of halonitrothiolene 1,1-dioxides: mono- and dihalo derivatives of 2,2,4-tri- and 2,4-dinitro-3-thiolene 1,1-dioxides. An X-ray diffraction study showed that 2,5-dinitro-2,3-dichloro-3-thiolene 1,1-dioxide molecules exist in the crystal as enantiomeric pairs; the five-membered rings have the *envelope* conformation, with deviation of the sulfur atom from the ring plane; the halogen atom and nitro group at the multiple bond are essentially coplanar with the ring.

2,2,4-Trinitrothiolene 1,1-dioxides [1] containing fragments of polynitroalkanes, CH acids, nitroethenes, and five-membered heterocycles are interesting polyfunctional objects. Owing to the presence in their molecules of several reaction centers, diverse reaction pathways are possible, allowing synthesis of previously unknown or difficultly accessible groups of compounds: dinitrothiolene 1,1-dioxides [2], arylaminodinitrobutadienes [3], substituted nitroquinoxalines [4], and also stable molecular complexes of dinitrothiophene 1,1-dioxides with pyridine ad its derivatives [5]. In view of the fact that introduction of a halogen atom into a nitrothiolene 1,1-dioxide ring considerably expands the synthetic potential of this class of compounds [1], it seemed interesting to prepare halo derivatives of di- and trinitrothiolene 1,1-dioxides and to reveal their structural features.

With the aim to prepare halogenated polynitrothiolene 1,1-dioxides, we studied nitration of 4-nitro-3-chloro-2- and -3-thiolene 1,1-dioxides **I** and **II**, and also of 2-hydroximino-3-chloro-3-thiolene 1,1-dioxide **III**. Nitration of **I**–**III** with 55% HNO_3 yielded 2,2,4-trinitro-3-chloro-3-thiolene 1,1-dioxide **IV**, but its yield did not exceed 8%. Along with the desired product **IV**, we obtained large amounts (~40%) of oxalic acid crystal hydrate, the well-known product of oxidative cleavage of haloethenes in nitration reactions [6, 7].



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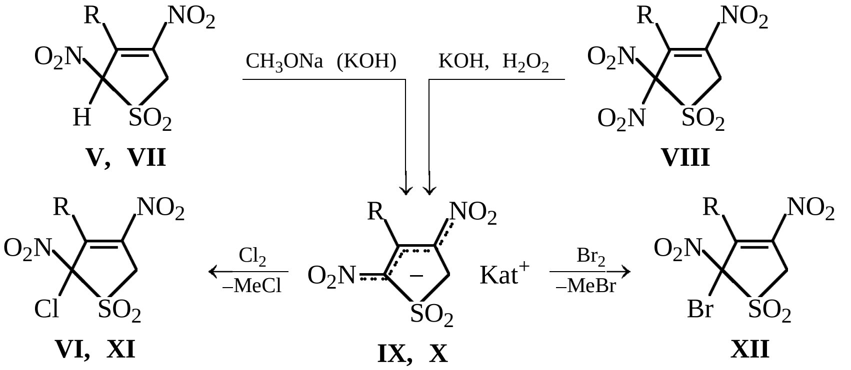
When varying the conditions of nitration of **II** with the aim to increase the yield of the desired product **IV**, we obtained unexpected results. With 100% nitric acid as nitrating agent (under these conditions, apparently, radical nitration is inhibited), we obtained a precursor of **IV**, 2,4-dinitro-3-chloro-3-thiolene 1,1-dioxide **V**. Under conditions of gradual increase in the nitrating agent concentration (the reaction was started in 55% HNO_3, and then 100% HNO_3 was added), we isolated 2,4-dinitro-2,3-dichloro-3-thiolene 1,1-dioxide **VI** in 6% yield, and also oxalic acid crystal hydrate. Apparently, compound **VI** formed under these conditions is a product of destructive nitration [8] associated with the effect of halogenating agents arising under the action of concentrated HNO_3 as oxidant on halogenated alkenes [9, 10].

A convenient route to dichlorodinitrothiolene 1,1-dioxide **VI** and to its structural analogs, 2-chloro- and 2-bromo-3-methyl-2,4-dinitro-3-thiolene 1,1-dioxides **XI** and **XII**, is halogenation of thiolenylnitronates [11]. Chlorination and bromination of 4(2)-nitro-1,1-dioxo-1λ^6-thiolenyl-2(4)-nitronates **IX** and **X**, which are prepared from di- and trinitro-containing precursors **V**, **VII**, and **VIII** [2], occurs under mild conditions and gives halo derivatives **VI**, **XI**, and **XII** in 25–34% yields as final products. The selectivity of the electrophilic attack of the C^2 position of **IX** and **X**, observed in these reactions, is characteristic of ambident thiolenylnitronate anions [11] and is probably due to the electron-withdrawing effect of the sulfonyl group on the electron density distribution:



R = Cl (**V**, **VI**, **IX**), CH_3 (**VII**, **VIII**, **X**–**XII**); Kat = Na (**IX**), K (**X**).

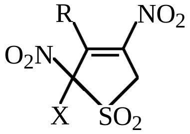
The spectral characteristics of 2,2,4-trinitro-3-cloro-3-thiolene 1,1-dioxide **IV** prepared by nitration of **I** and **III** are in agreement with published data [12] for the sample prepared by us from chloronitrothiolene 1,1-dioxide **II**; compounds **VII** and **X** were characterized in part in [2]. The structure of previously unknown compounds **V**, **VI**, **IX**, **XI**, and **XII** was determined spectroscopically (Table 1).

2,4-Dinitro-3-chloro-3-thiolene 1,1-dioxide **V** is a colorless crystalline substance; its ^1H NMR spectrum in DMSO-d_6 contains signals of the methylene (4.44 ppm) and nitromethine (8.39 ppm) protons. The downfield location of the latter signal is typical of similar dinitro compounds [13], including previously described 3-methyl-2,4-dinitro-3-thiolene 1,1-dioxide **VII** (8.50 ppm) [2], and is indicative of the increased CH acidity of dinitrothiolene 1,1-dioxides. The IR spectrun of **V** contains, along with the absorption bands of conjugated and nonconjugated nitro groups, also the bands of the ionized nitro group, indicating that the ionic structure contributes to the ground state of **V** (Table 1).

The spectral characteristics of sodium 4(2)-nitro-3-chloro-1,1-dioxo-1λ^6-thiolenyl-2(4)-nitronate **IX** agree with those of the previously described potassium salt of 3-methyl-2,4-dinitrothiolene 1,1-dioxide **X** [2]. The electronic absorption spectrum of **IX** in aqueous solution is characterized by a long-wave absorption band at λ_{max} 360 nm (ε 6000 l mol^{-1} cm^{-1}) corresponding to the conjugated heterocyclic dinitro anion. The IR spectrum contains absorption bands belonging to the ionized nitro group (1590, 1510, 1230, 1180 cm^{-1}) [14], sulfonyl group (1350, 1130 cm^{-1}), and multiple bond (1610 cm^{-1}).

2-Halo-2,4-dinitro-3-thiolene 1,1-dioxides **VI**, **XI**, and **XII** are light yellow crystalline substances with similar IR spectra (Table 1) containing bands of the C=C bond and nitro and sulfonyl groups. According to published data [14–16], the bands at 1590–1580 and 1310–1300 cm^{-1} can be assigned to vibrations of the *gem*-halonitromethyl group, the bands at 1540–1530 and 1360–1350 cm^{-1}, to vibrations of the conjugated nitro group, and the absorption in the range

Table 1. Physicochemical and spectral characteristics of substituted 2,4-dinitro-3-thiolene 1,1-dioxides **IV**–**VII**, **XI**, and **XII**



Comp. no.	R	X	Yield, %	mp, °C	IR spectrum,[a] ν, cm^{-1}			^1H NMR spectrum,[b] δ, ppm		
					$=CNO_2$, $C=NO_2^-$, $C(NO_2)X$	SO_2	C=C	CH_3	CH_2	$CHNO_2$
IV	Cl	NO_2	8	83–84	1600, 1590, 1550, 1390, 1330, 1320	1330, 1170	1640	–	4.93	–
V	Cl	H	25	141–142	1590, 1520, 1350, 1310, 1240, 1160	1350, 1130	1620	–	4.44	8.39
VI	Cl	Cl	34[c]	84–85	1590, 1540, 1350, 1310, 1200, 1160	1340, 1130	1620	–	4.93	–
VII	CH_3	H	50	76–77	1580, 1500, 1340, 1320, 1220, 1180	1340, 1120	1630	2.30	4.24	8.50
XI	CH_3	Cl	30	101–102	1590, 1530, 1350, 1300, 1220, 1200	1350, 1150	1600	2.20	4.27	–
XII	CH_3	Br	25	103–105	1580, 1540, 1360, 1300, 1210, 1170	1360, 1130	1610	2.40	4.30	–

[a] For measuring the IR spectra, samples of **IV** and **VII** were prepared as Nujol mulls, and samples of **V**, **VI**, **XI**, and **XII**, as KBr pellets. [b] The ^1H NMR spectra of **V** and **VII** were taken in DMSO-d_6, and those of **IV**, **VI**, **XI**, and **XII**, in acetonitrile-d_3. [c] The yield of **IV** is given for the synthesis by halogenation of **IX**.

Table 2. Atomic coordinates in the structure of **VI**, equivalent isotropic temperature factors of nonhydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$ ($Å^2$), and isotropic temperature factors of hydrogen atoms B_{iso} ($Å^2$)

Atom	**VIa**				**VIb**			
	x	*y*	*z*	B, B_{iso}	*x*	*y*	*z*	B, B_{iso}
Cl^2	–0.3489(4)	0.0556(8)	0.1443(2)	4.8(1)	0.2597(4)	0.3793(8)	–0.0086(2)	4.7(1)
Cl^3	–0.2600(3)	–0.3894(8)	0.0922(1)	4.26(9)	0.1098(3)	–0.0689(8)	0.0157(2)	4.1(1)
S^1	–0.2238(3)	–0.1194(7)	0.2288(1)	3.05(8)	0.3470(3)	0.3662(7)	0.0892(2)	3.30(9)
O^1	–0.3010(8)	–0.129(2)	0.2676(4)	3.7(2)	0.4730(8)	0.393(2)	0.0905(4)	3.7(2)
O^2	–0.1522(8)	0.081(2)	0.2182(3)	3.6(2)	0.2671(9)	0.560(2)	0.0909(5)	5.7(3)
O^3	–0.4089(9)	–0.485(2)	0.2091(5)	6.7(4)	0.4430(9)	–0.080(2)	0.0508(4)	6.1(3)
O^4	–0.5257(8)	–0.223(2)	0.1847(5)	7.9(5)	0.4516(9)	0.080(3)	–0.0163(3)	5.4(3)
O^5	0.0421(7)	–0.614(2)	0.1820(4)	3.9(3)	0.135(1)	–0.115(2)	0.1684(4)	7.0(3)
O^6	–0.061(1)	–0.664(2)	0.1207(4)	4.4(3)	0.0216(9)	–0.164(2)	0.1100(5)	5.9(4)
N^2	–0.4330(9)	–0.305(2)	0.1897(4)	3.6(3)	0.414(1)	0.061(2)	0.0215(5)	3.4(3)
N^4	–0.0482(8)	–0.580(2)	0.1582(4)	2.2(3)	0.110(1)	–0.098(2)	0.1262(5)	4.0(3)
C^2	–0.314(1)	–0.189(3)	0.1756(5)	3.7(4)	0.298(1)	0.204(2)	0.0367(4)	2.0(3)
C^3	–0.229(1)	–0.341(2)	0.1488(5)	1.7(3)	0.198(1)	0.065(2)	0.0544(5)	2.1(3)
C^4	–0.140(1)	–0.421(2)	0.1754(5)	2.6(3)	0.197(1)	0.039(3)	0.1017(5)	3.1(4)
C^5	–0.127(1)	–0.373(3)	0.2241(5)	2.8(3)	0.292(1)	0.172(3)	0.1296(5)	3.2(4)
H^{51}	–0.0183	–0.3279	0.2380	6	0.2373	0.2135	0.1631	6
H^{52}	–0.1449	–0.5027	0.2430	3	0.3656	0.0999	0.1436	4

1540–1530 and 1220–1160 cm^{-1}, apparently, to vibrations of the ionized nitro group.

The ^1H NMR spectrum of 2,4-dinitro-2,3-dichloro-3-thiolene 1,1-dioxide **VI** cosists of a single signal of methylene protons at 4.93 ppm. The spectra of 2-chloro- and 2-bromo-3-methyl-2,4-dinitro-3-thiolene 1,1-dioxides **XI** and **XII** contain signals of methyl (2.20, 2.40 ppm) and methylene (4.27, 4.30 ppm) protons. The UV spectrum of bromodinitrothiolene 1,1-dioxide **XII** contains an absorption band at λ_{max} 370 nm (ε 6000 l mol^{-1} cm^{-1}) characteristic of the 3-methyl-2,4-dinitro-3-thiolene 1,1-dioxide anion (λ_{max} 370 nm, ε 8000 l mol^{-1} cm^{-1} [2]). This fact suggests ready heterolytic rupture of the C–Br bond, which is consistent with published data for bromotrinitromethane [15] and for other *gem*-bromonitro derivatives [14, 16].

Table 3. Bond lengths (*d*, Å) in **VIa** and **VIb**

Bond	**VIa**	**VIb**	Bond	**VIa**	**VIb**	Bond	**VIa**	**VIb**
$\mathrm{Cl^2{-}C^2}$	1.77(2)	1.72(1)	$\mathrm{S^1{-}C^5}$	1.87(2)	1.75(2)	$\mathrm{N^2{-}C^2}$	1.53(2)	1.59(2)
$\mathrm{Cl^3{-}C^3}$	1.68(1)	1.68(1)	$\mathrm{O^3{-}N^2}$	1.25(2)	1.23(2)	$\mathrm{N^4{-}C^4}$	1.47(2)	1.44(2)
$\mathrm{S^1{-}O^1}$	1.40(1)	1.388(9)	$\mathrm{O^4{-}N^2}$	1.14(1)	1.17(2)	$\mathrm{C^2{-}C^3}$	1.52(2)	1.47(2)
$\mathrm{S^1{-}O^2}$	1.47(1)	1.46(1)	$\mathrm{O^5{-}N^4}$	1.22(1)	1.24(2)	$\mathrm{C^3{-}C^4}$	1.33(2)	1.36(2)
$\mathrm{S^1{-}C^2}$	1.86(2)	1.87(1)	$\mathrm{O^6{-}N^4}$	1.20(2)	1.14(2)	$\mathrm{C^4{-}C^5}$	1.43(2)	1.54(2)

Table 4. Bond angles (ω, deg) in **VIa** and **VIb**

Angle	**VIa**	**VIb**	Angle	**VIa**	**VIb**	Angle	**VIa**	**VIb**
$\mathrm{O^1S^1O^2}$	121.2(6)	119.9(7)	$\mathrm{O^5N^4O^6}$	122.0(1)	123.0(1)	$\mathrm{N^2C^2C^3}$	112.0(1)	112.0(1)
$\mathrm{O^1S^1C^2}$	108.7(6)	111.6(6)	$\mathrm{O^5N^4C^4}$	118.0(1)	112.0(1)	$\mathrm{Cl^3C^3C^2}$	118.0(9)	118.0(1)
$\mathrm{O^1S^1C^5}$	111.5(6)	113.5(7)	$\mathrm{O^6N^4C^4}$	120.0(1)	124.0(1)	$\mathrm{Cl^3C^3C^4}$	130.0(1)	126.0(1)
$\mathrm{O^2S^1C^2}$	107.4(7)	105.9(7)	$\mathrm{Cl^2C^2S^1}$	109.9(9)	110.8(8)	$\mathrm{C^2C^3C^4}$	112.0(1)	115.0(1)
$\mathrm{O^2S^1C^5}$	110.9(6)	108.0(7)	$\mathrm{Cl^2C^2N^2}$	109.5(9)	108.8(9)	$\mathrm{N^4C^4C^3}$	123.0(1)	124.0(1)
$\mathrm{C^2S^1C^5}$	93.3(7)	94.8(7)	$\mathrm{Cl^2C^2C^3}$	112.0(1)	115.5(9)	$\mathrm{N^4C^4C^5}$	113.0(1)	119.0(1)
$\mathrm{O^3N^2O^4}$	128.0(1)	128.0(1)	$\mathrm{S^1C^2N^2}$	110.0(1)	105.9(8)	$\mathrm{C^3C^4C^5}$	124.0(1)	117.0(1)
$\mathrm{O^3N^2C^2}$	110.0(1)	113.0(1)	$\mathrm{S^1C^2C^3}$	102.8(9)	103.5(9)	$\mathrm{S^1C^5C^4}$	100.3(9)	104.0(1)
$\mathrm{O^4N^2C^2}$	122.0(1)	119.0(1)						

Table 5. Torsion angles (ω, deg) in **VIa** and **VIb**

Angle	**VIa**	**VIb**	Angle	**VIa**	**VIb**
$\mathrm{O^1S^1C^2Cl^2}$	103.0(8)	–94.0(8)	$\mathrm{O^4N^2C^2C^3}$	–134(2)	125(1)
$\mathrm{O^1S^1C^2N^2}$	–18(1)	24(1)	$\mathrm{O^5N^4C^4C^3}$	167(1)	172(1)
$\mathrm{O^1S^1C^2C^3}$	–137.4(9)	141.6(9)	$\mathrm{O^5N^4C^4C^5}$	–17(2)	–9(2)
$\mathrm{O^2S^1C^2Cl^2}$	–29.9(9)	38.1(8)	$\mathrm{O^6N^4C^4C^3}$	–10(2)	–16(2)
$\mathrm{O^2S^1C^2N^2}$	–150(1)	155.9(8)	$\mathrm{O^6N^4C^4C^5}$	167(1)	163(1)
$\mathrm{O^2S^1C^2C^3}$	90(1)	–86(1)	$\mathrm{Cl^2C^2C^3Cl^3}$	–46(1)	46(1)
$\mathrm{C^5S^1C^2Cl^2}$	–143.0(8)	148.5(7)	$\mathrm{Cl^2C^2C^3C^4}$	135(1)	–141(1)
$\mathrm{C^5S^1C^2N^2}$	96(1)	–93.8(9)	$\mathrm{S^1C^2C^3Cl^3}$	–164.5(7)	167.7(8)
$\mathrm{C^5S^1C^2C^3}$	–23(1)	24(1)	$\mathrm{S^1C^2C^3C^4}$	17(1)	–19(1)
$\mathrm{O^1S^1C^5C^4}$	134.6(9)	–137.4(9)	$\mathrm{N^2C^2C^3Cl^3}$	78(1)	–79(1)
$\mathrm{O^2S^1C^5C^4}$	–87(1)	87(1)	$\mathrm{N^2C^2C^3C^4}$	–101(1)	94(1)
$\mathrm{C^2S^1C^5C^4}$	23(1)	–21(1)	$\mathrm{Cl^3C^3C^4N^4}$	–1(2)	–5(2)
$\mathrm{O^3N^2C^2Cl^2}$	176(1)	–176(1)	$\mathrm{Cl^3C^3C^4C^5}$	–177(1)	177(1)
$\mathrm{O^3N^2C^2S^1}$	–64(1)	65(1)	$\mathrm{C^2C^3C^4N^4}$	177(1)	–177(1)
$\mathrm{O^3N^2C^2C^3}$	50(2)	–47(2)	$\mathrm{C^2C^3C^4C^5}$	1(2)	4(2)
$\mathrm{O^4N^2C^2Cl^2}$	–9(2)	–4(2)	$\mathrm{N^4C^4C^5S^1}$	165.0(9)	–164(1)
$\mathrm{O^4N^2C^2S^1}$	112(2)	–123(1)	$\mathrm{C^3C^4C^5S^1}$	–19(2)	14(2)

Reliable information on the structure of 2,4-dinitro-2,3-dichloro-3-thiolene 1,1-dioxide **VI**, formed by this unusual pathway, is furnished by single crystal X-ray diffraction (Tables 2–5). We found that compound **VI** exists in the crystal as an enantiomeric pair of molecules **VIa** and **VIb** (Fig. 1) with the *R* and *S* configuration of C^2, respectively. The respective bond lengths and bond angles in crystallographically independent molecules **VIa** and **VIb** are equal within experimental error (Tables 3, 4).[1]

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[1] Because of the small size of the available crystal of **VI**, the number of the measured intensities was insufficient for full structure refinement, and the molecular geometries were determined with large errors. Therefore, we discuss only the molecular conformations.

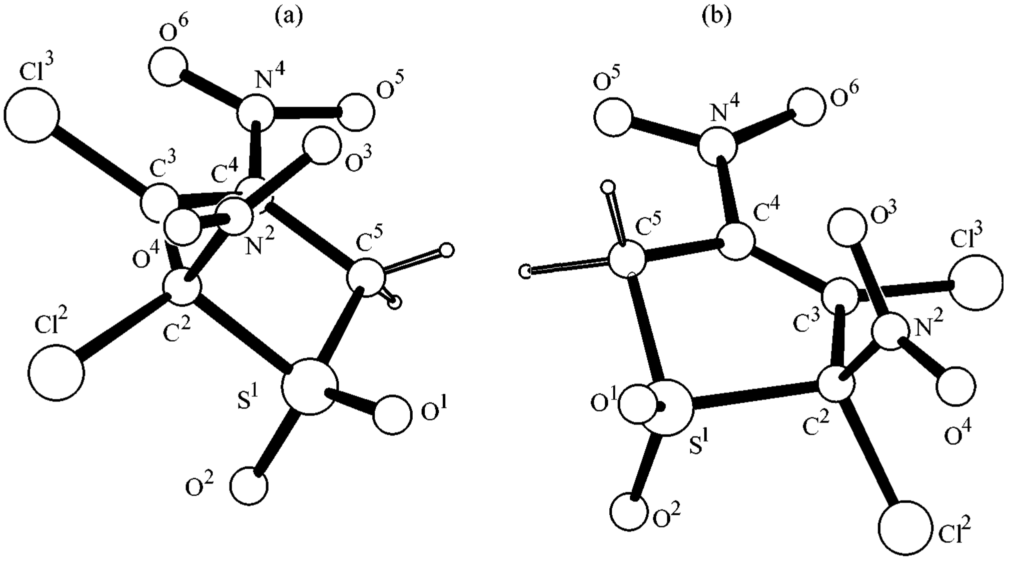

Fig. 1. Geometry of independent molecules (a) **VIa** and (b) **VIb** in the crystal.

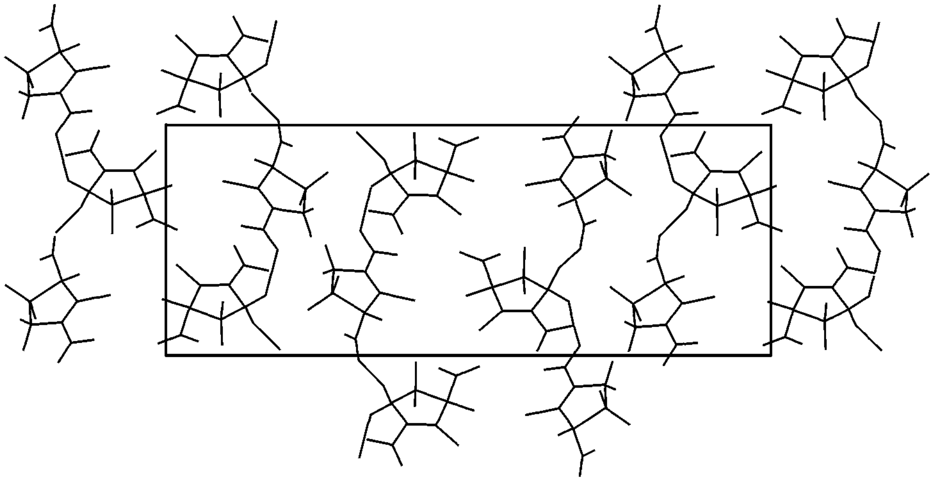

Fig. 2. Molecular packing of **VI** in the crystal (projection along the 0*x* axis). The C–H···O hydrogen bonds are shown.

The five-membered rings in **VIa** and **VIb** have the *envelope* conformation: The $C^2C^3C^4C^5$ fragments are planar within 0.005(14) (in **VIa**) and 0.02(2) Å (in **VIb**), and the sulfur atom deviates from this plane by 0.560(4) (in **VIa**) and −0.510(4) Å (in **VIb**). The O^2 atoms at sulfur and the nitro groups at C^2 are axial, and the O^1 and Cl^2 atoms are equatorial. The double bond in the rings of **VIa** and **VIb** has a usual planar structure, despite the eclipsed location of such bulky substituents as Cl and NO_2 [torsion angle $Cl^3C^3C^4N^4$ –1(2)° in **VIa** and –5(2)° in **VIb**] (Table 5). The nitro group at C^4 is also virtually coplanar with the double bond [torsion angle $C^3C^4N^4O^6$ –10(2)° in **VIa** and –16(2)° in **VIb**; dihedral angle between the $C^2C^3C^4C^5$ and $C^4N^4O^5O^6$ planes 12(2)° in **VIa** and 14(2)° in **VIb**]. There are short intramolecularr contacts between Cl^3 and O^6 [2.85(1) Å in **VIa** and 2.92(1) Å in **VIb**; sum of the van der Waals radii 3.27 Å]. The C^3–Cl^3 and C^4–N^4 bonds are appreciably shorter than the corresponding bonds at C^2, which is consistent with variation of the carbon covalent radius depending on the carbon valence state.

The molecular packing in the crystal (Fig. 2) is determined by C–H···O hydrogen bonds:

(1) C^{5a}–$H^{51a}\cdots O^{2a'}$ $(-x, -1/2 + y, 1/2 - z)$, C^{5a}–H^{51a} 1.28, $H^{51a}\cdots O^{2a'}$ 2.31, $C^{5a}\cdots O^{2a'}$ 3.481(15) Å, angle C^{5a}–$H^{51a}\cdots O^{2a'}$ 150°;

(2) C^{5b}–$H^{51b}\cdots O^{1a}$, C^{5b}–H^{51b} 1.16, $H^{51b}\cdots O^{1a}$ 2.31, $C^{5b}\cdots O^{1a}$ 3.181(19) Å, angle C^{5b}–$H^{51b}\cdots O^{1a}$ 130°;

(3) $C^{5b}–H^{51b}\cdots O^{5a''}$ ($–x$, $1/2 + y$, $–1/2 – z$), $C^{5b}–H^{51b}$ 1.16, $H^{51b}\cdots O^{5a''}$ 2.43, $C^{5b}\cdots O^{5a''}$ 3.377(16) Å, angle $C^{5b}–H^{51b}\cdots O^{5a''}$ 137°;

(4) $C^{5b}–H^{52b}\cdots O^{4a'''}$ ($1 – x$, $–1/2 + y$, $1/2 – z$), $C^{5b}–H^{52b}$ 1.00, $H^{52b}\cdots O^{4a'''}$ 2.57, $C^{5b}\cdots O^{4a'''}$ 3.481(19) Å, angle $C^{5b}–H^{52b}\cdots O^{4a'''}$ 153°.

Along with these hydrogen bonds, in the crystal of **VI** there are numerous short contacts (shorter than the sum of the van der Waals radii) between the Cl, O, and N atoms. As a result, the molecular packing is fairly close, which is manifested in the high density of **VI**, 1.95 g cm^{-3}.

Thus, we have developed new procedures for preparing mono- and dihalo derivatives of 2,2,4-trinitro- and 2,4-dinitro-3-thiolene 1,1-dioxides and characterized their structure by UV, ^{1}H NMR, and IR spectroscopy. The molecular geometry and structural parameters of 2,4-dinitro-2,3-dichloro-3-thiolene 1,1-dioxide have been determined by single crystal X-ray diffraction.

EXPERIMENTAL

The IR spectra were taken on Specord IR-75 and UR-20 spectrophotometers (LiF and NaCl prisms). Samples of **IV** and **VII** were prepared as Nujol mulls, and samples of **V**, **VI**, **XI**, and **XII**, as KBr pellets.

The electronic absorption spectra were taken on a Specord M-40 double-beam spectrophotometer (dismountable quartz cells) with automatic recording of the spectrum and on an SF-46 spectrophotometer (quartz cells). The solvents were water (for **IX**) and acetonitrile (for **XII**).

The ^{1}H NMR spectra were measured on a Tesla BS-487C spectrometer (80 MHz). The solvents were acetonitrile-d_3 for **IV**, **VI**, **VII**, **IX**, and **XII**, and DMSO-d_6 for **V**. The chemical shifts were determined relative to internal and external HMDS (accuracy ±0.5 Hz, δ scale).

4-Nitro-3-chloro-2-thiolene 1,1-dioxide **I** [17], 4-nitro-3-chloro-3-thiolene 1,1-dioxide **II** [18], 4-nitro-2-hydroximino-3-chloro-3-thiolene 1,1-dioxide **III** [19], and 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide **VIII** [20] were prepared by published procedures.

Light yellow crystals of **VI** were grown from the reaction solution. Rhombic system; at 20°C: a 10.930(5), b 6.030(5), c 28.642(8) Å; V 1888(1) Å^3, d_{calc} 1.95 g cm^{-3}, Z 8, space group $P2_12_12_1$ (two independent molecules **VIa** and **VIb**). The unit cell parameters and intensities of 4307 reflections, of which 1812 had $I \geq 3\sigma$, were measured on an Enraf-Nonius CAD-4 automatic four-circle diffractometer at 20°C in the reciprocal space quadrant (CuK_α radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 70°$). The intensities of three check reflections did not decrease in the course of the experiment. The absorption (μCu 85.66 cm^{-1}) was not taken into account empirically, because we found no sufficiently strong reflections with $\chi \geq 80°$. The structure was solved by the direct method using SIR program [21] and refined first in the isotropic and then in the anisotropic approximation. All the hydrogen atoms were subsequently revealed from the differential electron density series, and their contribution to the structural amplitudes was taken into account with fixed positional and isotropic temperature parameters. To elucidate the absolute structure, we refined the direct and inverted structures. For the direct structure, R 0.07276, R_W 0.07388; for the inverted structure, R 0.07523, R_W 0.07839. A total of 271 parameters were refined from 1322 reflections. According to the Hamilton test [22], the direct structure corresponds to the absolute structure with 90% probability. The final divergence factors are R 0.073, R_W 0.074 for 1322 unique reflections with $F^2 \geq 3\sigma$. All calculations were performed on an Alpha Station 200 computer using MolEN program package [23]. The figures were plotted and the intermolecular contacts analyzed using PLATON program [24].

2,2,4-Trinitro-3-chloro-3-thiolene 1,1-dioxide IV. *a*. Dinitrogen tetroxide (1 ml) was added to a solution of 1 g of 4-nitro-3-chloro-2-thiolene 1,1-dioxide **I** in 6 ml of 55% HNO_3. The mixture was left for 70 h, after which the solution was evaporated in the cold until light yellow crystals of **IV** formed; these crystals were filtered off and dried. Yield 0.11 g (7%), mp 83–84°C (from chloroform). Mixing with an authentic sample prepared according to [12][2] gave no melting point depression. Found, %: C 16.92, 16.91; H 0.90, 0.89; N 14.56, 14.56. $C_4H_2ClN_3O_8S$. Calculated, %: C 16.70; H 0.70; N 14.61. The mother liquor was further evaporated in the cold, and the residue was dried in a vacuum desiccator. Oxalic acid crystal hydrate was obtained; yield 0.53 g (42%), mp 100–102°C (from methanol) {mp 101.5°C (from water) [25]}.

b. Compound **IV** was prepared from 4-nitro-3-chloro-3-thiolene 1,1-dioxide **II** according to [12] in the absence of paraform. Yield 8%, mp 83–84°C (from chloroform).

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[2] The melting point of 2,2,4-trinitro-3-chloro-3-thiolene 1,1-dioxide **IV** prepared according to [12] is also 83–84°C and not 108°C as erroneously indicated in [12].

c. Dinitrogen tetroxide (1 ml) was added with stirring to a solution of 2.0 g of 4-nitro-2-hydroximino-3-chloro-3-thiolene 1,1-dioxide **III** in 10 ml of 55% HNO_3. The mixture was left for 1 h, after which the solution was evaporated in the cold until light yellow crystals of **IV** formed; these crystals were filtered off and dried. Yield 0.23 g (8%), mp 83–84°C (from chloroform). Mixing with the samples prepared by procedures *a* and *b* gave no melting point depression. The mother liquor was further evaporated in the cold, and the residue was dried in a vacuum desiccator. Oxalic acid crystal hydrate was obtained; yield 0.98 g (44%), mp 100–102°C (from methanol).

2,4-Dinitro-3-chloro-3-thiolene 1,1-dioxide V. A 2-g portion of **II** was dissolved in 20 ml of 100% HNO_3. The solution was left for 10 days, after which it was evaporated in the cold until colorless crystals of the initial 4-nitro-3-chloro-3-thiolene 1,1-dioxide **II** started to form; these crystals were filtered off and dried. A 0.26-g portion of **II** (13%) was recovered; mp 159–160°C. Mixing with the initial sample gave no depression of the melting point. The filtrate was further evaporated in the cold until light yellow plates of **V** formed; these were filtered off and dried in a vacuum desiccator. Yield of **V** 0.62 g (25%), mp 140–142°C. Found, %: C 19.89, 19.90; H 1.35, 1.40; N 9.69, 9.73. $C_4H_3ClN_2O_6S$. Calculated, %: C 19.79; H 1.24; N 9.90. The mother liquor was further evaporated in the cold, and the residue was dried in a vacuum desiccator. Oxalic acid crystal hydrate was obtained; yield 0.30 g (12%), mp 100–102°C (from methanol).

Sodium 4(2)-nitro-3-chloro-1,1-dioxo-1λ^6-thiolenyl-2(4)-nitronate IX. A solution of 0.33 g of sodium methylate in 5 ml of absolute methanol was added dropwise to a suspension of 0.72 g of 2,4-dinitro-3-chloro-3-thiolene 1,1-dioxide **V** in 25 ml of absolute ether. The solution was stirred for 15 min, after which the precipitate was filtered off, washed with absolute ether, and dried in a vacuum desiccator over alkali. Yield of sodium nitronate **IX** 0.63 g (78%), mp 165–168°C (dec.).

2,4-Dinitro-2,3-dichloro-3-thiolene 1,1-dioxide VI. *a*. A 2-g portion of **II** was dissolved in 15 ml of 55% HNO_3. After 24 h, 5 ml of 100% HNO_3 was added, and the mixture was left for 10 days. After that, the mixture was evaporated in the cold until yellow needles of **VI** formed, which were filtered off and dried. Yield 0.17 g (6%), mp 84–85°C. Found, %: C 17.22, 17.25; H 0.70, 0.69; N 9.63, 9.88. $C_4H_2Cl_2N_2O_6S$. Calculated, %: C 17.33; H 0.72; N 10.14. The mother liquor was further evaporated in the cold, and the residue was dried in a vacuum desiccator. Oxalic acid crystal hydrate was obtained; yield 0.56 g (22%), mp 100–102°C (from methanol).

b. Chlorine was passed through 0.79 g of a suspension of **IX** in 25 ml of absolute methanol. The salt gradually dissolved, and a white precipitate formed. After keeping for 30 min, the NaCl precipitate was filtered off, and the mother liquor was evaporated on a rotary evaporator. The light yellow oily residue was treated with chloroform to induce crystallization of **VI**. The light yellow crystals were filtered off and dried. Yield of **VI** 0.25 g (34%), mp 84–85°C (dec.). Mixing with the sample prepared by procedure *a* gives no melting point depression.

3-Methyl-2,4-dinitro-3-thiolene 1,1-dioxide VII. A 1-ml portion of 30% H_2O_2 was added to a suspension of 0.53 g of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide **VIII**. The resulting mixture was cooled to –10°C, after which a solution of 0.27 g of sodium ethylate in 10 ml of absolute ethanol was added dropwise. After keeping for 20 min, the solvent was evaporated in the cold, and the residue was dried in a vacuum desiccator. The resulting colorless precipitate was treated with 5 ml of anhydrous acetonitrile; the sodium nitrite precipitate was separated by decanting, and the solution was evaporated on a rotary evaporator. The resulting colorless crystals were dried in a vacuum desiccator. Yield of crystal hydrate of **VII** 0.32 g (73%), mp 76–77°C (dec.). Compound **VII** is unstable; therefore, it was purified by reprecipitation with dry chloroform from absolute acetone. Found, %: C 20.72, 20.70; H 4.94, 4.91; N 10.01, 10.10. $C_5H_6N_2O_6S \cdot 4H_2O$. Calculated, %: C 20.41; H 4.80; N 9.52.

Potassium 3-methyl-4(2)-nitro-1,1-dioxo-1λ^6-thiolenyl-2(4)-nitronate X. *a*. A 3-ml portion of 30% H_2O_2 was added to a solution of 0.53 g of **VIII** in 20 ml of methanol. The mixture was cooled to –10°C, and a solution of 0.80 g of KOH in 10 ml of methanol was added dropwise. After keeping for 10 min, the orange precipitate of nitronate **X** was filtered off. Yield 0.42 g (80%), decomposition point 170°C.

b. A solution of 0.17 g of KOH in 10 ml of methanol was added to a suspension of 0.88 g of crystal hydrate of **VII** in 10 ml of methanol. After keeping for 10 min, nitronate **X** was subjected to halogenation without intermediate isolation.

3-Methyl-2,4-dinitro-2-chloro-3-thiolene 1,1-dioxide XI. Chlorine was passed through a suspension of 0.78 g of **X** in 25 ml of absolute methanol. The red precipitate of the salt gradually dissolved, and a white precipitate formed. After keeping for 30 min, the KCl precipitate was filtered off, and the mother liquor was treated with chloroform, after which colorless crystals of **XI** were separated and air-dried. Yield 0.23 g (30%), 101–102°C (dec.). Found, %: C 23.06, 23.09; H 2.27, 2.27; N 11.09, 11.06. $C_5H_5ClN_2O_6S$. Calculated, %: C 23.39; H 1.95; N 10.92.

2-Bromo-3-methyl-2,4-dinitro-3-thiolene 1,1-dioxide XII. A solution of 0.21 ml of bromine in 5 ml of absolute methanol was added dropwise to a suspension of 0.78 g of **X** in 25 ml of absolute methanol, cooled to a temperature from –10 to –5°C. The mixture was stirred for an additional 30 min at the same temperature, after which the KBr precipitate was filtered off, and the mother liquor was evaporated in the cold. Light yellow crystals of **XII** formed, which were filtered off and dried in a vacuum desiccator over $CaCl_2$. Yield 0.48 g (54%), mp 103–105°C (dec.). Found, %: C 20.00, 20.04; H 2.00, 2.00; N 9.37, 9.40. $C_5H_5BrN_2O_6S$. Calculated, %: C 19.93; H 1.66; N 9.30.

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