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Synthesis and Structure of 3-Methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide

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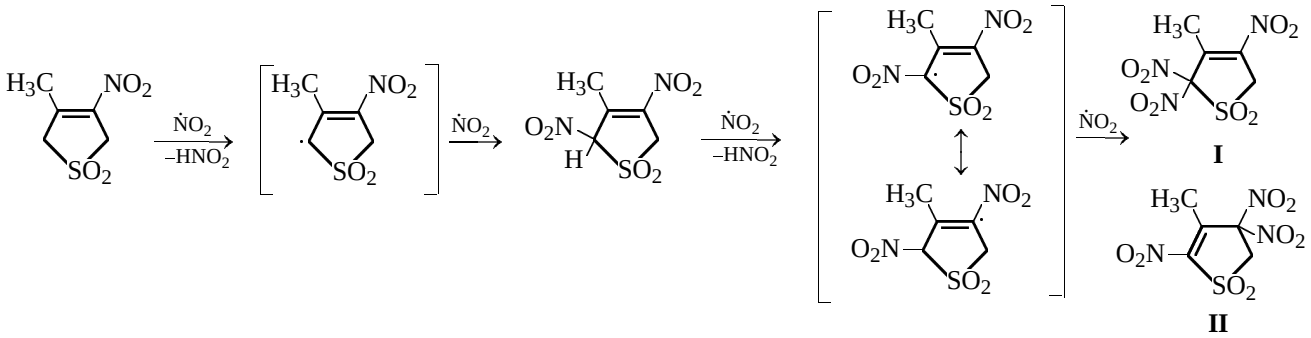
Abstract — The structure of the first representative of the polynitrothiolene 1,1-dioxide series was studied. Complex analysis of quantum-chemical results, spectral characteristics, and powder X-ray diffraction patterns allowed this compound to be assigned the structure of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide. The heteroring has an *envelope* conformation. The sulfur atom slightly deviates from the ring plane, the nitro group attached to the C_{sp^2} atom is involved in conjugation, and the nitro groups attached to the C_{sp^3} atom are nonequivalent and perpencular to each other.

Mononitrothiolene 1,1-dioxides have been found to exhibit diverse properties. They can react with nucleophilic, electrophilic, and radical reagents and are highly susceptible to cheletropic transformations [1, 2]. Polynitrothiolene 1,1-dioxides hold an even greater promise for synthesis. Representatives of this series, trinitrothiolene-1,1-dioxides, have been prepared by nitration of 4-nitro-3- and -2-thiolene 1,1-dioxides [2, 3].

Among trinitrothiolene 1,1-dioxides, the most readily accessible proved to be that containing methyl group at the heteroring C^3 atom [3]. It was synthesized by nitration of 3-methyl-4-nitro-3-thiolene 1,1-dioxide with 55% nitric acid. This homolytic process can give rise to two structural isomers **I** and **II** differing from each other in the mutual arrangement of the dinitromethyl and nitroethene fragments.



The ^1H and ^{13}C NMR, and IR spectral data of the resulting trinitrothiolene 1,1-dioxide $C_5H_5N_3O_8S$ (Table 1), as well as its behavior in reactions with nucleophiles allow no unambiguous decision between isomers **I** and **II**. Actually, the major conversion routes of the trinitrothiolene 1,1-dioxide in hand, involving HNO_2 cleavage with formation of 2,4-dinitrothiophene 1,1-dioxide as an intermediate product [4, 5] or NO cleavage to give finally 2,4-dinitrothiolene 1,1-dioxide salts [6, 7] are equally characteristic of **I** and **II**. Moreover, in view of the high energetic favorability of the resonance-stabilized radical (or anion) formed by NO cleavage, one should not exclude the possibility of mutual conversions of isomers

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Table 1. Spectral characteristics of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide (**I**) and 3-methyl-2,4,4-trinitro-2-thiolene 1,1-dioxide (**II**)

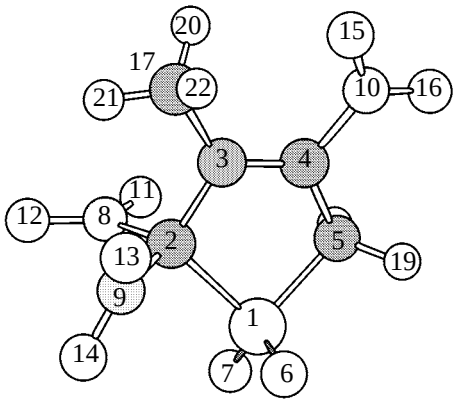
IR spectrum, ν, cm^{-1}				^1H NMR spectrum (CD_3CN), δ, ppm		Solid-state ^{13}C NMR spectrum, δ_C, ppm				
C=C	$=CNO_2$	$C(NO_2)_2$	SO_2	CH_3	CH_2	*A*, CH_3	*B*, CH_2	*C*, $C(NO_2)_2$	*D*, =CMe	*E*, $=CNO_2$
Experiment										
1600	1550, 1380	1600, 1580, 1330	1360, 1175	2.38	4.61	13	53	123	132	150
Calculation for isomer **I**										
						19	61	134	149	157
Calculation for isomer **II**										
						16	63	122	147	163

I and **II** in the reaction medium.

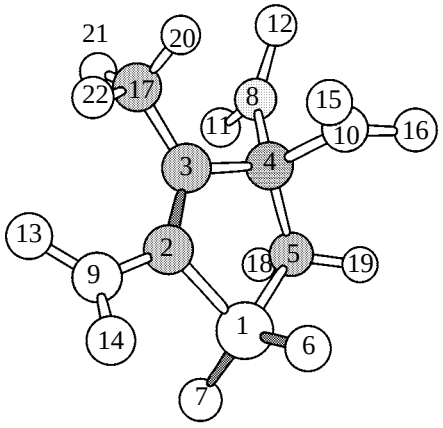
To evaluate the relative stability of the isomeric forms of the trinitrothiolene 1,1-dioxide, we performed theoretical calculations of both isomer **I** and isomer **II**. The calculations were performed by the GAUSSIAN 98 program [8] by the HF method with the 6-31G* basis set and by the B3PW91 density functional method with the gradient-corrected exchange functional of Becke [9] and inclusion of electron correlation effects [10]. The standard 6-311+G* basis set was chosen for all atoms. Geometry optimization at both the theoretical levels resulted in similar molecular geometries and lack of imaginary vibration frequencies, which corresponds to an energy minimum. According to the calculations, the energy of isomer **I** is only 0.56 kcal/mol higher than that of isomer **II**.

The geometric parameters of molecules **I** and **II** gain insight into structural features of these forms (Fig. 1, Table 2). The shortest interatomic distances in isomers **I** and **II** are listed in Table 3. From the resulting geometric parameters we calculated ^{13}C NMR spectra (Table 1). The chemical shifts were related to tetramethylsilane [T_d symmetry; *d*(Si–C) 1.8869, *d*(C–H) 1.0951 Å]. Geometry optimization of tetramethylsilane was performed at the B3PW91/6-311+G* level. A slightly better fit of calculation to the solid-state ^{13}C NMR spectrum was observed for isomer **I**.

The calculated vibration frequencies of structures **I** and **II** involved no imaginary values. The theoretical IR spectra of isomers **I** and **II** worse fit experimental in the range 1340–1390 cm^{-1} characteristic of symmetric stretching vibrations of nitro groups (conjugated and unconjugated), as well as of asymmetric stretching vibrations of SO_2 groups. The calculation



I



II

Fig. 1. Molecular models of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide (**I**) and 3-methyl-2,4,4-trinitro-2-thiolene 1,1-dioxide (**II**) as given by B3PW91/6-311+G* *ab initio* calculations.

Table 2. Principal geometric parameters (bond lengths, Å, and bond angles, deg) and relative energies (kcal/mol) of molecules **I** and **II** as given by B3PW91/6-311+G* *ab initio* calculations

Parameter[a]	**I**	**II**	Parameter[a]	**I**	**II**
S^1–C^2	1.907	1.808	N^{10}–O^{15}	1.216	1.209
S^1–C^5	1.813	1.826	N^{10}–O^{16}	1.220	1.206
S^1=O^7	1.445	1.448	$C^2S^1C^5$	92.2	90.6
S^1=O^6	1.451	1.450	$O^6S^1O^7$	122.4	121.8
C^3–/=C^4	1.345	1.520	$S^1C^2C^3$	105.5	115.1
C^2=/–C^3	1.500	1.336	$C^2C^3C^4$	111.5	111.1
C^5–C^4–/=	1.490	1.512	$C^3C^4C^5$	121.7	111.2
C^3–C^{17}	1.496	1.492	$S^1C^5C^4$	103.4	105.3
C^2–N^8	1.536	–	ON^8O	127.9	128.6
C^2–N^9	1.521	1.453	ON^9O	127.9	126.8
C^4–N^8	–	1.556	$N^8C^2N^9$	109.2	–
C^4–N^{10}	1.464	1.547	$N^8C^4N^{10}$	–	105.7
N^8–O^{11}	1.210	1.208	$O^{12}N^8CN$	16.6	–19.8
N^8–O^{12}	1.204	1.205	$O^{13}N^9C^2C^3$	0.0	26.5
N^9–O^{13}	1.209	1.217	$O^{15}N^{10}C^4C^3$	16.7	–8.6
N^9–O^{14}	1.206	1.214	$S^1C^5C^4C^3$	–17.1	–26.3
Ee	0.56	0.0	*IMG*	0	0
Ee + *Ezpe*	0.47	0.0			

[a] *Ee* + *Ezpe* is the sum of the electron and zero-point enegries and *IMG* is the number of imaginary frequencies.

places in this range three strong bands (1395, 1380, and 1358 cm^{-1}) for isomer **II** and only two (1388 and 1377 cm^{-1}) for molecule **I**. The calculated frequencies of structure **I** better fit the experimental IR spectrum (Table 1).

Thus, by theoretical calculations we obtained structural and energetic characteristics of isomers **I** and **II**. However, the resulting data, which proved quite close for the two isomers, allowed neither isomer to be preferred, regardless of the high level of the calculation methods used [11].

The solid-state structure of the trinitrothiolene 1,1-dioxide in hand was unambiguously determined by powder X-ray diffraction. The latter method was chosen, since we failed to obtain crystals appropriate for single-crystal X-ray diffraction analysis.

The unit cell parameters (Table 4) were measured in an FR-552 Guinier chamber (Cu$K_{\alpha1}$ radiation, bent Ge monochromator) using the TREOR90 indexing program [13]. The *Pna*2_1 space group was assigned on the basis of systematic extinctions. The intensities for solving and refining the structure were measured on a Stoe STADI-P powder diffractometer (Cu$K_{\alpha1}$ radiation, bent Ge monochromator, linear position-sensitive detector, transmission mode). The molecular models of **I** and **II**, obtained by the MOPAC 7.2 program [14], were used in solving the crystal structure by the systematic search technique [15]. The solution was found with model **I**, which was confirmed by the subsequent Rietveld refinement by the MRIA program [16]. The resulting refined molecular structure is shown in Fig. 2, the atomic coordinates[1] are given in Table 5, and the experimental and calculated X-ray diffraction patterns are depicted in Fig. 3.

Table 3. Short distances (*l*, Å) in molecules **I** and **II** as given by B3PW91/6-311+G* *ab initio* calculations

I		**II**	
distance	*l*	distance	*l*
S^1···O^{11}	3.046	S^1···O^{14}	2.937
S^1···O^{14}	3.020	C^3···O^{15}	2.672
C^3···O^{13}	2.749	C^5···O^{11}	2.762
C^3···O^{15}	2.797	N^{10}···O^{12}	2.594
C^5···O^{16}	2.651	O^{11}···H^{18}	2.298
N^9···O^{12}	2.654	O^{13}···H^{22}	2.364
O^{15}···H^{20}	2.434	O^{16}···H^{19}	2.419

Table 4. Crystal data for molecule **I**

Parameter	Value
Formula	$C_5H_5N_3O_8S$
Syngony	Orthorhombic
Space group	*Pna*2_1
a, Å	13.999(3)
b, Å	11.806(3)
c, Å	5.979(2)
M_{20}	44
F_{30}	71 (0.009, 48)
V, $Å^3$	988.2(5)
Z	4
d_{calc}, g/cm^3	1.796
2χ range, deg	8—80
Number of reflexes	340
R_p[a]	0.024
R_{wp}[a]	0.031
R_{exp}[a]	0.015

[a] The R_p, R_{wp}, and R_{exp} values were obtained in [12].

[1] All structural data (including X-ray diffraction puttern) are deposited in the Cambridge structural database (no. CCDC 165956) and can be requested in CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033. E-mail: deposit@ccdc.cam.ac.uk].

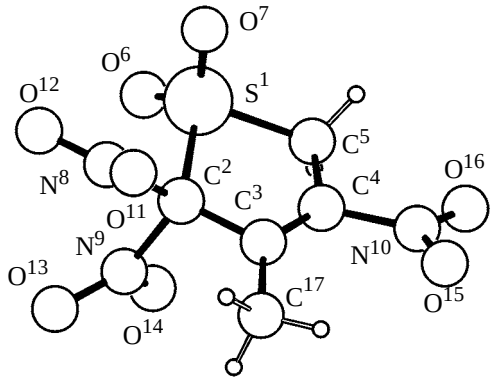


Fig. 2. Molecular structure of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide (**I**) as given by powder X-ray diffraction.

As follows from the X-ray powder diffraction data, the molecule in study is sterically strained, which shows up first of all in increased bond lengths: S^1–C^2 1.903(8), S^1–C^5 1.805(8), C^2–N^8 1.54(1), and C^2–N^9 1.52(1) Å (Table 6) {cf. standard values 1.765 and 1.485 Å, respectively [17]}. At the same time, the calculated bond lengths are close to those [S^1–C^2 1.86(2), S^1–C^5 1.87(2), and C^2–N 1.53(2) Å] in 2,3-dichloro-2,4-dinitro-3-thiolene 1,1-dioxide [18]. The conformation of the five-membered ring is *envelope*. The deviation of the sulfur atom from the mean plane defined by the C^2 (0.02 Å), C^3 (–0.03 Å), C^4 (0.03 Å), and C^5 (–0.02 Å) atoms is –0.058 Å (Table 7). The pucker parameters after Cremer and Pople [19] are as follows: *q*2 0.03235(1) and *Phi* –8.86(2). The $N^{10}O^{15}O^{16}$ group is turned with respect to the double bond by 16°. The shortest intermolecular contact C^5–$H^{19}\cdots O^{15}$ (*–x*, *–y*, 1/2 + *z*) is 2.58 Å, and the $C^5H^{19}\cdots O^{15}$ angle is 117.5°.

Table 5. Atomic coordinates and thermal parameters (U_{iso}, Å) for structure **I**

Atom	*x*	*y*	*z*	U_{iso}
S^1	0.2062(1)	0.2014(1)	0.2119(3)	0.026(2)
C^2	0.1300(5)	0.3062(6)	0.0487(9)	0.054(6)
C^3	0.0659(3)	0.2361(5)	0.0919(1)	0.037(6)
C^4	0.1018(5)	0.1278(5)	0.1290(8)	0.042(7)
C^5	0.1902(5)	0.0972(5)	0.0058(8)	0.042(5)
O^6	0.3013(2)	0.2373(2)	0.2268(6)	0.045(3)
O^7	0.1511(2)	0.1716(3)	0.4045(6)	0.038(3)
N^8	0.0827(3)	0.3788(3)	0.2310(9)	0.068(5)
N^9	0.1913(3)	0.3850(5)	0.091(8)	0.065(5)
N^{10}	0.0523(3)	0.0443(3)	0.2659(8)	0.068(4)
O^{11}	0.0004(3)	0.3819(2)	0.2364(8)	0.083(4)
O^{12}	0.1398(2)	0.4271(3)	0.3485(8)	0.068(4)
O^{13}	0.1764(3)	0.4838(3)	0.0907(8)	0.092(5)
O^{14}	0.2493(3)	0.3379(2)	0.2060(5)	0.061(4)
O^{15}	0.0298(3)	0.0620(3)	0.3166(9)	0.083(3)
O^{16}	0.1058(3)	0.0343(3)	0.3033(8)	0.064(4)
C^{17}	0.0119(5)	0.2955(5)	0.214(1)	0.072(6)
H^{18}	0.244(3)	0.102(3)	0.125(5)	0.05
H^{19}	0.189(2)	0.019(3)	0.035(5)	0.05
H^{20}	0.033(3)	0.257(3)	0.335(6)	0.05
H^{21}	0.014(2)	0.371(2)	0.257(5)	0.05
H^{22}	0.061(2)	0.312(3)	0.102(5)	0.05

Note that the experimental geometric parameters of trinitrothiolene dioxide **I** nicely fit the calculated bond lengths and angles for isomer **I** (Tables 2, 3, 6, and 7). For instance, the calculated and experimental C_{sp^2}–N bond lengths both reveal conjugation of the nitro group and are 1.464 and 1.456 Å, respectively (Tables 2 and 6), and the calculated angle that relates to deviation of the NO_2 group from the double-bond plane, diverges from experimental by as little as 0.7° (Tables 2 and 7). Comparison of the experimental and calculated C_{sp^3}–N bond lengths points to nonequivalence of the NO_2 groups attached to the heteroring C_{sp^3} atom: One of the C_{sp^3}–NO_2 bonds is longer than the other by 0.02 Å (Tables 2 and 3) and longer than a normal C_{sp^3}–NO_2 bond [17, 20]. This finding apparently explains the enhanced tendency of the compound in hand to NO_2 or HNO_2 cleavage [4–7].

Generally, the complex analysis of the results of quantum-chemical calculations and powder X-ray diffractometry allowed us to unambiguously assign the sample in hand the structure of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide (**I**) in the solid state and to characterize its geomety. The heteroring in compound **I** has an *envelope* conformation; the sulfur atom deviates for the sulfur plane; the NO_2 groups attached to the C_{sp^3} atom are nonequivalent and perpendicular to each other.

Table 6. Bond lengths (*d*, Å) in molecule **I**

Bond	*d*	Bond	*d*
S^1–C^2	1.903(7)	N^8–O^{11}	1.164(6)
S^1–C^5	1.805(6)	N^8–O^{12}	1.207(6)
S^1–O^6	1.400(3)	N^9–O^{13}	1.185(7)
S^1–O^7	1.430(4)	N^9–O^{14}	1.200(6)
C^2–C^3	1.482(8)	N^{10}–O^{15}	1.207(6)
C^2–N^8	1.537(8)	N^{10}–O^{16}	1.213(6)
C^2–N^9	1.517(8)	C^5–H^{18}	1.04(4)
C^3–C^4	1.392(8)	C^5–H^{19}	0.96(3)
C^3–C^{17}	1.486(8)	C^{17}–H^{20}	0.90(4)
C^4–C^5	1.485(9)	C^{17}–H^{21}	1.00(3)
C^4–N^{10}	1.457(7)	C^{17}–H^{22}	0.98(3)

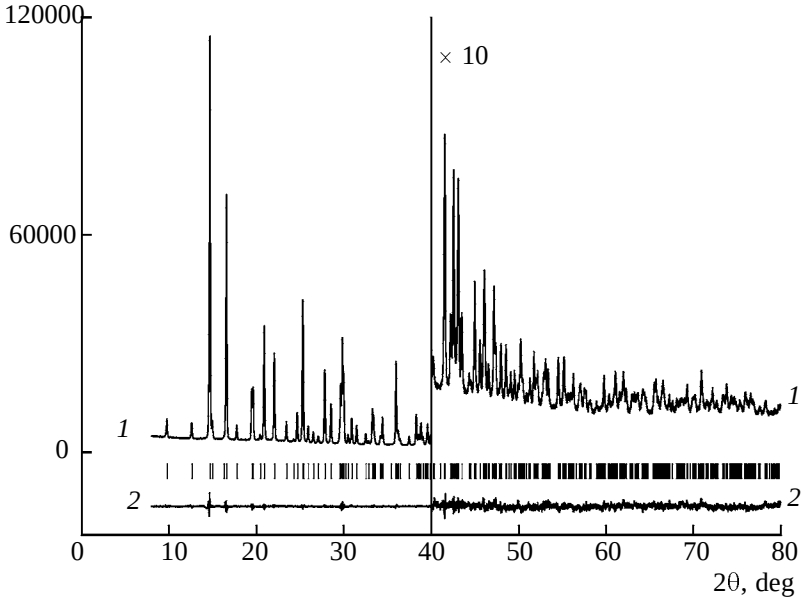


Fig. 3. (*1*) Experimental and (*2*) difference X-ray pattern after the final Rietveld refinement of the solved structure. Calculated positions of reflexes are shown by vertical lines.

Table 7. Bond lengths (ω, deg) in molecule **I**

Angle	ω	Angle	ω
C^2SC^5	90.2(3)	$C^4C^5H^{22}$	110.0(2)
$C^2S^1O^6$	111.7(3)	$C^2N^8O^{11}$	117.9(4)
$C^2S^1O^7$	105.7(2)	$C^2N^8O^{12}$	113.0(4)
$C^5S^1O^6$	111.7(3)	$O^{11}N^8O^{12}$	129.1(4)
$C^5S^1O^7$	110.3(2)	$C^2N^9O^{13}$	120.2(5)
$O^6S^1O^7$	122.4(2)	$C^2N^9O^{14}$	114.5(4)
$C^3C^2N^8$	116.9(4)	$O^{13}N^9O^{14}$	125.3(5)
$C^3C^2N^9$	111.8(5)	$C^4N^{10}O^{15}$	118.5(5)
$C^3C^2S^1$	105.5(3)	$C^4N^{10}O^{16}$	109.1(4)
$N^8C^2N^9$	107.0(4)	$O^{15}N^{10}O^{16}$	132.0(4)
$N^8C^2S^1$	103.9(4)	$S^1C^5H^{21}$	112.0(2)
$C^2C^3C^4$	112.6(4)	$S^1C^5H^{22}$	119.0(2)
$C^2C^3C^{17}$	117.3(4)	$H^{18}C^5H^{19}$	104.0(3)
$C^4C^3C^{17}$	128.3(4)	$C^3C^{17}H^{20}$	113.0(2)
$C^3C^4C^5$	116.5(5)	$C^3C^{17}H^{21}$	106.0(2)
$C^3C^4N^{10}$	122.7(4)	$C^3C^{17}H^{22}$	106.0(2)
$C^5C^4N^{10}$	120.7(5)	$H^{20}C^{17}H^{21}$	111.0(3)
$C^4C^5S^1$	107.2(4)	$H^{20}C^{17}H^{22}$	114.0(3)
$C^4C^5H^{21}$	104.0(2)	$H^{21}C^{17}H^{22}$	105.0(3)

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer in chloroform in the frequency ranges of LiF and NaCl prisms. The ^{1}H NMR spectra (in acetonitrile-d_3) were obtained on a Bruker Ac-200 spectrometer (200 MHz). The solid-state ^{13}C NMR spectra were taken on a Bruker instrument (100 MHz). The chemical shifts were measured in δ with an accuracy of ±0.5 Hz.

3-Methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide (I). 3-Methyl-4-nitro-3-thiolene 1,1-dioxide, 5 g, was mixed with 65 ml of 55% nitric acid, and the reaction mixture was allowed to stand under hood. Nitrogen oxides evolved, and the starting compound gradually dissolved. After 48 h, the precipitate was filtered off, washed with cold water, and dried in a vacuum over calcium chloride to obtain 2.39 g (32%) of 3-methyl-2,2,4-trinitro-3-thiolene 1,1-dioxide (**I**), mp 104–105°C (decomp., dry chloroform).

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