

Synthesis and crystal structure of 5,5'-dinitro-[5,5'-bi-(1,3,2-dioxathiane)]2,2'-dioxide

Pan Zhang, Jia-Rong Li, De-Li Yang and Da-Xin Shi*

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, P.R. China

A novel 1,3,2-dioxathiane-2-oxide derivative 5,5'-dinitro-[5,5'-bis(1,3,2-dioxathiane)]2,2'-dioxide was synthesised. Moreover, the molecular structure of the compound was confirmed by the X-ray crystal structure determination.

Keywords: 1,3,2-dioxathiane-2-oxide, synthesis, X-ray structure

1,3,2-Dioxathiane-2-oxide is a type of cyclic sulfite which possesses reducibility and could be oxidised to sulfates. This kind of compound is a preservative for black and white developing agents¹ and antioxidants.^{2,3} More commonly, sulfates are used as additives to improve the first discharge capacity and cycling performance in lithium ion battery.^{4,5} Some synthetic methods for sulfites have been reported.^{6–10} We now report the synthesis and crystal structure of the title compound (Table 1).

Thionyl chloride is a chlorinated reagent which is usually used in the chlorination of hydroxyl groups. During the chlorination of alcohol **4** using thionyl chloride as chlorinated reagent, a white solid, instead of the expected chlorated derivative **6**, was obtained. Its structure was characterised as 5,5'-dinitro-[5,5'-bis(1,3,2-dioxathiane)]2,2'-dioxide by IR, ¹H NMR, ¹³C NMR, elemental analyses and X-ray diffraction (Scheme 1).

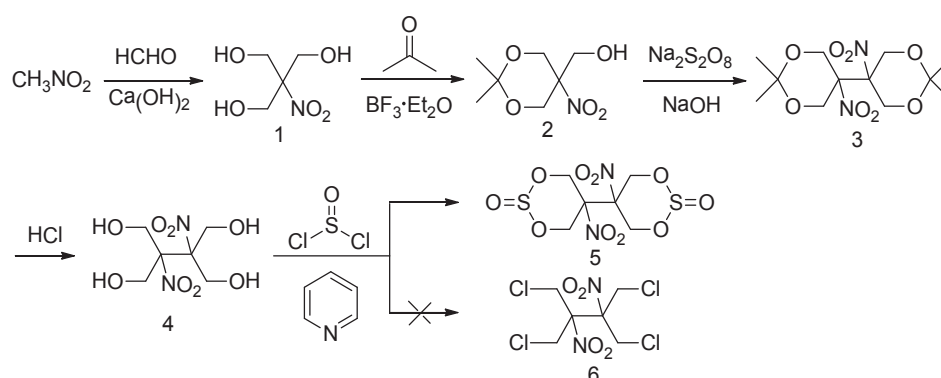
Results and discussion

The synthetic route to 5,5'-dinitro-[5,5'-bis(1,3,2-dioxathiane)]2,2'-dioxide is outlined in Scheme 1. Compounds **1** to **4** were synthesised according to the literature.^{11,15} In the catalysis of calcium hydroxide, compound **1** was obtained by the condensation of nitromethane with formaldehyde. Protection of two hydroxyl groups by acetone gave compound **2**. Reaction between compound **2** and sodium hydroxide generated the nitronate salt of **2**, and then homocoupling of the nitronate salt in the presence of sodium persulfate gave compound **3**.¹² Compound **4** was obtained by deketalisation in the presence of concentrated hydrochloric acid. We tried to use thionyl chloride to prepare chlorinated product **6**, but a white solid was obtained after the reaction mixture was diluted with ice water. The melting point of the white solid is 194 °C. In the IR spectrum, 1568, 1332 cm⁻¹ were the stretching vibration of nitro groups, and disappearance of the absorption peak of hydroxyl groups showed that they were substituted by other

groups. In the ¹H NMR spectrum, the signals appearing at δ 4.88 and 5.44 ppm were assigned to the two protons of methylene, which indicated that they were in different chemical environment. Finally, the structure of the solid was confirmed to be cycle sulfite **5** by X-ray diffraction.

Table 1 Crystallographic data and structure refinement for the title compound

5	
Empirical formula	C ₆ H ₈ N ₂ O ₁₀ S ₂
Formula weight	332.26
Temperature/K	100.1
Wavelength/Å	0.71070
Crystal size/mm	0.15 × 0.40 × 0.40
Crystal system	Monoclinic
Space group	C2/c
Volume/Å ³	1127.8(2)
Z	4
Calculated density/Mg·m ⁻³	1.957
Unit cell dimensions	$a=8.5392(9)$ Å $\alpha=90.00^\circ$ $b=10.9002(11)$ Å $\beta=101.595(11)^\circ$ $c=12.3692(14)$ Å $\gamma=90.00^\circ$
Absorption coefficient/mm ⁻¹	0.533
Max. and min. transmission	1.00000 and 0.83089
F(000)	680
Crystal size/mm	0.15 × 0.40 × 0.40
θ range for data collection	3.26 to 26.00°
Limiting indices	$-10 \leq h \leq 10, -9 \leq k \leq 13, -15 \leq l \leq 9$
Reflection collected/unique	2050/1112
Completeness to $\theta=25.05$	99.67
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1112/0/91
Goodness of fit F^2	1.270
Final R indices ($I > 2\sigma(I)$)	R = 0.0838, wR = 0.2169
R indices (all data)	R = 0.0900, wR = 0.2196
Largest diff. peak and hole/e Å ⁻³	1.22 and -0.65



Scheme 1 Synthesis of the title compound **5**.

* Correspondent. E-mail: jrli@bit.edu.cn

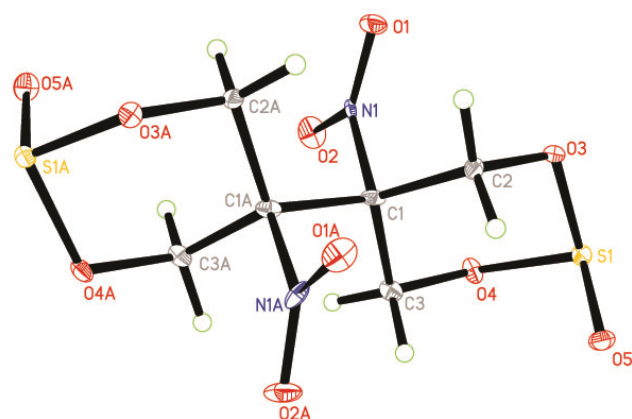


Fig. 1 Molecular structure of compound **5** at 30% probability thermal ellipsoids.

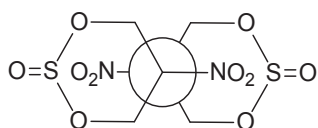


Fig. 2 Newman projection of compound **5**.

As shown in the Fig. 1, the molecule is made up of two six-membered heterocyclic rings, which exist in a chair conformation with the S=O group axially oriented.^{13,14} This shows that the energy of the title compound with chair conformation is lower than that of title compound with other conformations. In the six-membered ring, atoms O3, C2, O4 and C3 are not in one plane. Two nitro groups exist with staggered conformation from Newman projection (Fig. 2). In the molecule, all bond distances are normal, and all C atoms are of sp³ hybridisation, while the bond angles of C(2)–C(1)–C(1A), C(3)–C(1)–C(1A) and N(1)–C(1)–C(1A) are different from 109.5° with the influence of the nitro group (Table 2).

Interestingly, there exists only one kind of H proton in the methylene of the title compound, while the different chemical shifts of the two protons in the ¹H NMR spectrum can be seen from Fig. 3. In the analysis of some analogous structures, according to Takeo Sato and Bi Fu-Qiang,^{15,16} the difference exists because of the function of steric configuration, while the methylene protons experience magnetic nonequivalence.

Apart from this explanation, hydrogen bonds may be used to explain the different chemical shifts of H atoms of the methylene. In the methylene, only one H atom participates hydrogen bond, resulting in the difference of chemical environment of the two H atoms.

As shown in Fig. 3, there exists in the crystal lattice two kinds of potential weak intermolecular interactions of C–H...O, which are summarised in Table 3, only one H atom of the methylene participates in the hydrogen bonds.

Table 2 Selected bond lengths (Å) and bond angles (°)

Bond	Dist.	Bond	Dist.
S(1)–O(4)	1.628(5)	O(4)–C(3)	1.449(7)
S(1)–O(3)	1.623(4)	O(3)–C(2)	1.444(7)
S(1)–O(5)	1.444(5)	C(1)–C(1A)	1.601(12)
Angle	(°)	Angle	(°)
O(3)–S(1)–O(4)	96.9(2)	C(2)–O(3)–S(1)	114.5(4)
O(5)–S(1)–O(4)	107.1(3)	O(4)–C(3)–C(1)	108.8(5)
O(5)–S(1)–O(3)	107.2(2)	O(3)–C(2)–C(1)	108.4(5)
C(3)–O(4)–S(1)	115.2(4)	C(2)–C(1)–C(1A)	112.2(4)
C(3)–C(1)–C(1A)	112.4(4)	N(1)–C(1)–C(1A)	105.7(6)

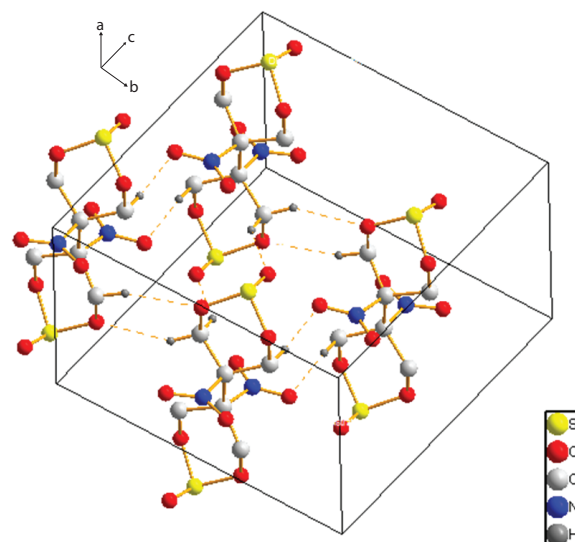


Fig. 3 Packing diagram of 5,5'-dinitro-[5,5'-bi(1,3,2-dioxathiane)]2,2'-dioxide.

In conclusion, we have synthesised a novel 1,3,2-dioxathiane-2-oxide derivative and its structure was characterised by IR, ¹H NMR, ¹³C NMR and X-ray crystal analysis.

Experimental

All commercial reagents and solvents were purchased and used without further purification. Melting points were determined using XT4A microscope melting point apparatus (uncorrected). IR spectra were recorded on a PerkinElmer FT-IR spectrophotometer with KBr pellets. ¹H and ¹³C NMR spectra were recorded at a Varian mercury-plus 400 spectrometer with TMS as the internal standard. Elemental analyses (C, H and N) were performed on a Flash EA 1112 elemental analyser.

General procedure

2,3-Bis(hydroxymethyl)-2,3-dinitro-1,4-butanediol **4** (4 mmol) was dissolved in 6 mL of thionyl chloride. Then pyridine (2 mL) was added to the solution and the system were refluxed for 4 h. The reaction mixture was added dropwise to ice water (100 mL) immediately under magnetic stirring, and white solid was precipitated. After stirring for a few minutes, the solid was washed with water for several times. Then filtration gave the product and it was recrystallised from MeOH to give white crystalline powder. The colourless single crystal suitable for X-ray diffraction analysis was obtained by diffusion of petroleum ether when the compound was dissolved in ethyl acetate for a few days.

5,5'-Dinitro-[5,5'-bis(1,3,2-dioxathiane)]2,2'-dioxide (**5**): Solid, yield: 75%, m.p. 194 °C; IR (KBr, cm⁻¹): 1568, 1332 (NO₂); ¹H NMR: (400 MHz, DMSO-d₆) δ_H 4.88 (d, 4H, J=12.8 Hz, CH₂), 5.44 (d, 4H, J=13.2 Hz, CH₂); ¹³C NMR: (100 MHz, DMSO-d₆) δ_C 56.77, 87.90. Anal. calcd for C₆H₈N₂O₁₀S₂: C, 21.69; H, 2.43; N, 8.43; found: C, 21.47; H, 2.45; N, 8.18%.

Crystal structure determination of 5,5'-dinitro-[5,5'-bi(1,3,2-dioxathiane)]2,2'-dioxide (**5**): Suitable single crystals of **5** for X-ray structural analysis were obtained by recrystallisation from petroleum/ethyl acetate. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated Mo

Table 3 Hydrogen bond lengths (Å) and bond angles (°)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA
C(2)–H(2B)...O(1) ^a	0.990	2.568	3.555(8)	174.914
C(3)–H(3A)...O(5) ^b	0.990	2.394	3.244(8)	143.542
C(3)–H(3B)...O(3) ^c	0.990	2.456	3.340(8)	148.483
C(2)–H(2A)...O(4) ^d	0.990	2.501	3.387(8)	148.775

D and A are the hydrogen-bond donor and acceptor, respectively.

K α radiation ($\lambda=0.71070$ Å) at 100.1 K. The structures were solved by direct methods with SHELXS-97 program and refinements on F^2 were performed with SHELXL-97¹⁷ program by full-matrix least-squares techniques. Crystallographic data of **5** (CCDC1007542) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

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