

КРАТКИЕ СООБЩЕНИЯ

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FACILE SYNTHESIS AND CRYSTAL STRUCTURE OF
1,5-DIMETHYL-6-THIOXO-1,3,5-TRIAZINANE-2,4-DIONEN. Shajari¹, A.R. Kazemizadeh¹, A. Ramazani¹, S.W. Joo²,
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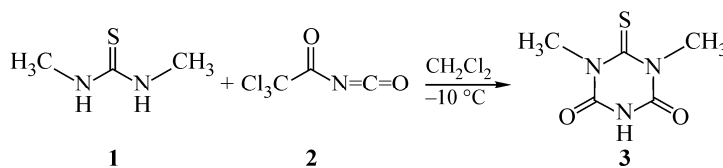
The title compound 1,5-dimethyl-6-thioxo-1,3,5-triazinane-2,4-dione $C_5H_7N_3O_2S$ is synthesized *via* the reaction between N,N'-dimethylthiourea and trichloroacetyl isocyanate in dichloromethane. The structure of the title compound is characterized by IR, ¹H NMR, ¹³C NMR, elemental analysis, and single-crystal X-ray diffraction. The crystal structure reveals the role of N—H···O and C—H···O hydrogen bonds, and C=O···π interactions in the arrangement of the molecules into ribbons, which are further joined to each other to form double-layers parallel to the (001) plane.

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Heterocyclic compounds have great importance in the biological and medicinal sciences and thus there are many efforts for the development of new efficient and mild synthetic routes for their synthesis [1, 2]. Triazine derivatives have fungicide [3], antiplasmodial [4], anti-HIV [5], and herbicidal [6] activities. They also have application in protection of amino groups [7] as well as for the synthesis of polyamines [8] and polyfunctional amino alcohols [7]. In connection with our interest to the synthesis of heterocycles [9—13], we report the reaction between N,N'-dimethylthiourea (**1**) and trichloroacetyl isocyanate (**2**) to produce 1,5-dimethyl-6-thioxo-1,3,5-triazinane-2,4-dione (**3**). The crystal structure of **3** was determined by X-ray diffraction. Compound (**3**) was synthesized long ago [14], however in the Cambridge structural database there are no data on the structure of neutral 6-thioxo-1,3,5-triazinane-2,4-dione derivatives [14].

Experimental. Materials and apparatuses. Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured on an electrothermal 9100 apparatus and were uncorrected. IR spectra were measured on a Jasco FT-IR 6300 spectrometer. ¹H and ¹³C NMR spectra were measured (CDCl₃ solution) with a BRUKER DRX-250 AVANCE spectrometer at 250.0 MHz and 62.5 MHz respectively. Elemental analyses were performed using a Heraeus CHN-O-rapid analyzer.



Scheme 1. Synthesis of 1,5-dimethyl-6-thioxo-1,3,5-triazinane-2,4-dione

Synthesis and characterization of compound 3. Title compound **3** was synthesized by the method depicted in Scheme 1. To a magnetically stirred solution of trichloroacetyl isocyanate **2** (1 mmol) in 5 ml CH_2Cl_2 *N,N'*-dimethylthiourea **1** (1 mmol) was added at $-10\text{ }^\circ\text{C}$. The mixture was stirred at room temperature for 4 h. Then the mixture was filtered and washed with CH_2Cl_2 . The remaining white solid was dissolved in 5 ml chloroform and refluxed for 8 h. The solvent was removed under reduced pressure and washed with CH_2Cl_2 . Single crystals were obtained by slow evaporation using a *n*-heptane/chloroform (1:4, v/v) solvent system.

Yield 80 %, white powder, m.p. $190.1 \sim 191.2\text{ }^\circ\text{C}$, Anal. Calcd. (%) for $\text{C}_5\text{H}_7\text{N}_3\text{O}_2\text{S}$ (173.19): C, 34.67; H, 4.07; N, 24.26. Found (%): C, 34.62; H, 4.10; N, 24.29. IR (KBr) ν/cm^{-1} : 3249 (NH), 1712(C=O), 1465, 1119, 764. ^1H NMR (250 MHz, CDCl_3) δ/ppm : 3.69 (*s*, 6H, 2 CH_3), 9.54 (*bs*, 1H, NH). ^{13}C NMR (62.5 MHz, CDCl_3) δ/ppm : 35.74 (2 CH_3), 147.24 (C=S), 178.54 (2C=O).

Crystal structure determination. The crystallographic measurement was performed on an Oxford Diffraction Xcalibur with a PX κ -geometry four-circle diffractometer with graphite-monochromatized MoK_α radiation. The data were collected at 120(2) K using an Oxford Cryosystems cooler. Data collection, cell refinement, and data reduction and analysis were carried out with the Xcalibur PX software, CRYCALIS CCD, and CRYCALIS RED respectively [15]. Empirical absorption correction was applied to the data with the use of CRYCALIS RED. The structures were solved by direct methods using the SHELXS-97 program [16] and refined by a full-matrix least-squares technique based on F^2 using SHELXL-97 [16] with anisotropic thermal parameters for the non-H-atoms. The H atoms were found in difference Fourier maps and were refined isotropically. The figures presenting the molecular and crystal structures were made using the DIAMOND program [17]. CCDC-886361 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for (3). $\text{C}_5\text{H}_7\text{N}_3\text{O}_2\text{S}$, $M = 173.20$, colorless block, crystal size $0.34 \times 0.28 \times 0.18\text{ mm}$, monoclinic, space group $P2_1/n$ (no. 14), $a = 7.249(2)\text{ \AA}$, $b = 7.357(2)\text{ \AA}$, $c = 14.082(4)\text{ \AA}$, $\beta = 100.76(4)^\circ$, $V = 737.8(4)\text{ \AA}^3$, $T = 120(2)\text{ K}$, $Z = 4$, $\rho_{\text{calc}} = 1.559\text{ g/cm}^3$, $\mu = 0.39\text{ mm}^{-1}$ (for MoK_α , $\lambda = 0.71073\text{ \AA}$), absorption correction: multi-scan, $T_{\text{min}} = 0.947$, $T_{\text{max}} = 1.000$, 14990 reflections measured, 4030 unique ($R_{\text{int}} = 0.021$), 3273 observed ($I > 2\sigma(I)$), θ range $4.43\text{--}38.53^\circ$, parameters = 128, restraints = 0, $R_1 = 0.030$, $wR_2 = 0.086$ (observed refl.), $\text{GOOF} = S = 1.08$, largest difference in peak and hole, $\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}} = 0.49$ and -0.34 e/\AA^3 .

Results and discussion. The reaction between **1** and **2** led to **3**. The ^1H NMR, ^{13}C NMR, and IR for the product are in good agreement with the title compound.

The structure of compound **3** was also confirmed by a single crystal X-ray structure determination (Fig. 1). This *N,N'*-dimethylthiocyanuric acid is a planar molecule (with an r.m.s. deviation of fitted non-H atoms = 0.029 \AA). The values of bond lengths and valence angles (Table 1) correspond well with those typical of the respective types of chemical bonds [18]. It should be noted that the bond lengths are also very

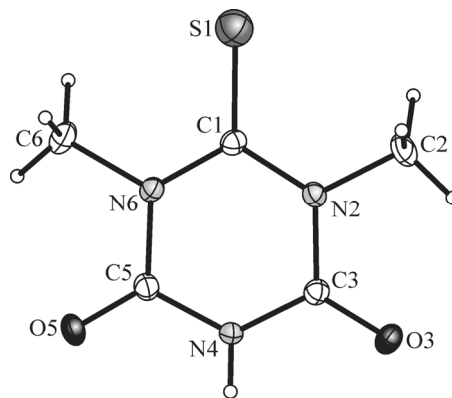


Fig. 1. View of the molecule of **3** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level

Selected geometric parameters (Å, deg.) for **3**

Bond lengths		Bond angles			
S(1)—C(1)	1.6548(7)	C(1)—N(2)—C(2)	119.17(6)	N(6)—C(1)—S(1)	121.76(5)
O(3)—C(3)	1.2186(8)	C(1)—N(2)—C(3)	123.67(5)	N(2)—C(1)—N(6)	116.36(5)
O(5)—C(5)	1.2212(8)	C(2)—N(2)—C(3)	116.75(6)	O(3)—C(3)—N(2)	122.88(6)
N(2)—C(1)	1.3782(9)	C(5)—N(4)—C(3)	125.72(6)	O(3)—C(3)—N(4)	122.03(6)
N(2)—C(2)	1.4696(9)	C(1)—N(6)—C(5)	123.37(6)	N(4)—C(3)—N(2)	115.09(6)
N(2)—C(3)	1.3901(9)	C(1)—N(6)—C(6)	119.10(5)	O(5)—C(5)—N(4)	121.41(6)
N(4)—C(3)	1.3688(9)	C(5)—N(6)—C(6)	117.25(6)	O(5)—C(5)—N(6)	123.11(6)
N(4)—C(5)	1.3663(9)	N(2)—C(1)—S(1)	121.88(5)	N(4)—C(5)—N(6)	115.48(6)
N(6)—C(1)	1.3827(9)				
N(6)—C(5)	1.3850(9)				
N(6)—C(6)	1.4733(9)				

close to the corresponding bond lengths of 2-(2,4-dioxo-6-thioxo-(1,3,5)triazinan-1-yl)ethylammonium chloride and bromide salts [19].

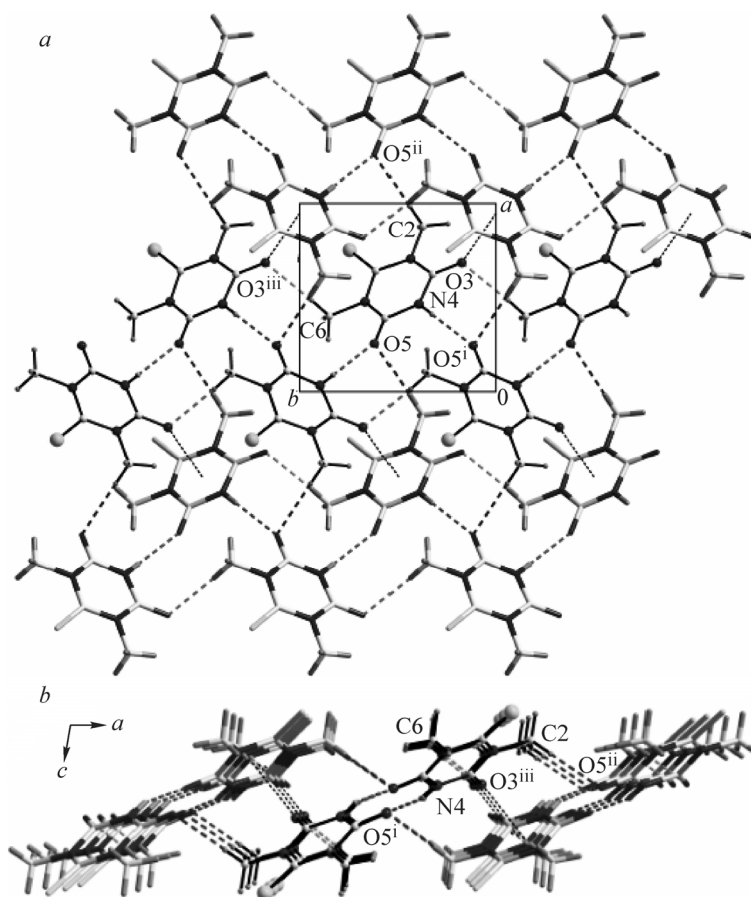


Fig. 2. Three ribbons (shown with different styles) joined *via* the inter-ribbon C—H···O and C=O··· π interactions to form doublelayers parallel to (001) plane in the crystal of **3**. Viewed down the *c* axis (*a*) and *b* axis (*b*). Symmetry codes are given in Table 2

Table 2

Hydrogen bond geometry (Å, deg.) for (3)

$D-H\cdots A$	$D-H$, Å	$H\cdots A$, Å	$D\cdots A$, Å	$D-H\cdots A$, deg.
N4—H4 \cdots O5 ⁱ	0.83(2)	2.10(2)	2.895(1)	159(2)
C2—H2C \cdots O5 ⁱⁱ	0.97(2)	2.47(2)	3.440(2)	179(1)
C6—H6A \cdots O3 ⁱⁱⁱ	0.96(2)	2.38(2)	3.337(2)	176(2)

Symmetry codes: (i) $-x+1/2, y-1/2, -z+3/2$; (ii) $x+1, y, z$; (iii) $x, y+1, z$.

The crystal structure of (3) is stabilized by a network of intermolecular N—H \cdots O and C—H \cdots O hydrogen bonds and C=O \cdots π interactions linking the adjacent molecules (Fig. 2, Table 2). Ribbons along the b axis are generated by means of N—H \cdots O and C—H \cdots O contacts linking the adjacent molecules in a manner shown in Fig. 2. This combination of the action of 2_1 screw axis and a direct b axis translation gives rise to $R_3^3(13)$ rings within the ribbon.

As shown in Fig. 2, the adjacent ribbons, related by a direct a axis translation are linked to each other *via* other C—H \cdots O interactions to form double-layers parallel to the (001) plane, at $z = 1/4, 3/4, \dots$. Within the inter-ribbon contacts there are also C=O \cdots π interactions (dotted lines in Fig. 2) with an O \cdots Cg(1) distance of 2.794(1) Å, perpendicular to the O \cdots ring separation of 2.749 Å, C=O \cdots Cg(1) angle of 142.28(6)° and C \cdots Cg(1) = 3.831(2) Å [Cg(1) is the ring centroid].

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