

The Crystal Structure of 2-Thiohydantoin, C₃H₄ON₂S*

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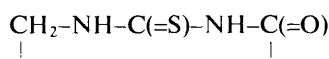
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The crystal structure of the monoclinic form of 2-thiohydantoin has been determined from three-dimensional photographic X-ray data. The space group is $P2_1/c$; $a = 5.635$, $b = 11.503$, $c = 7.469$ Å, $\beta = 99^\circ 29'$, and there are four molecules in the unit cell. The structure was derived from Patterson and electron density maps and refined by least squares methods. The final residual R for 1037 independent reflections is 0.094. The planar molecules are bonded together by hydrogen bonds in infinite sheets approximately parallel to the (102) plane.

Introduction

The crystal structure of 2-thiohydantoin



is one of several investigations carried out on this laboratory on chelate compounds and organic compounds forming chelates. 2-Thiohydantoin reacts with silver(I) (Dubský, Šindelář & Černák, 1938) in the same manner as rhodanine, whose structure was determined earlier (van der Helm, Lessor & Merritt, 1962). The aim of this research program is to determine the structure of the silver complex and compare it to that of the precipitating agent, although so far all attempts at crystallizing the precipitates of either silver rhodanide or silver 2-thiohydantoin have failed. This is possibly due to polymerization as has been proposed by Stephen & Townshend (1965).

Experimental

First attempts at recrystallization of 2-thiohydantoin were from hot water and yielded a triclinic modification in the form of yellow needles. Most of the crystals however, were twinned. Later, single crystals suitable for X-ray investigation were grown by slow evaporation of a saturated ethanol solution. When grown in this manner the crystals are dark yellow rods with a diamond-shaped cross section. They show a pronounced cleavage plane at about 60° to the rod axis, which is the a axis.

From oscillation and Weissenberg photographs the reciprocal lattice symmetry was found to be $2/m$ (C_{2h}). The systematic extinction of $h0l$ reflections when l is odd and of $0k0$ when k is odd identified the space group as $P2_1/c$ (No. 14). Unit-cell dimensions were found

from zero-level Weissenberg (Cu $K\alpha$) and precession photographs (Mo $K\alpha$):

$$a = 5.635 \pm 0.007, b = 11.503 \pm 0.007, c = 7.469 \pm 0.010 \text{ \AA}$$

$$\beta = 99^\circ 29' \pm 6'$$

The assumption of four molecules of C₃H₄ON₂S per unit cell leads to a calculated density of 1.615 g.cm⁻³, in good agreement with the observed value of 1.595 g.cm⁻³, measured by flotation.

Multiple film equi-inclination Weissenberg photographs of levels Hkl for $1 \leq H \leq 2$, hKl for $0 \leq K \leq 10$, and hkL for $0 \leq L \leq 6$ were collected using Cu $K\alpha$ radiation. The three different crystals used during the data collection were fragment cleaved off the rods. They were selected as equidimensional as possible and were parallelepipeds whose largest dimension was 0.5 mm. The intensities were estimated visually with the use of standard scales prepared from characteristic reflections. A total of 1037 independent diffraction maxima were recorded. Of these, 89 were too weak to be observed and were assigned one-half the minimum observed intensity for the range. The preliminary data processing was carried out with the use of programs written for the IBM 709 and the CDC 3600 computers. An estimate of the standard error of each reflection was made from the original intensity readings; this value was later modified according to the actual agreement obtained in the final merging of the different data sets. In order to avoid accidental agreement which would put undue weight on a few reflections, a minimum standard error of $0.5 \times$ (the average standard error for the set) was imposed. No corrections for absorption or extinction were made, ($\mu_{\text{Cu}K\alpha} = 52.5$ cm⁻¹). Preliminary scale and temperature factors were estimated by Wilson's method.

Structure determination and refinement

The structure was solved entirely from the Patterson function. The three-dimensional Patterson function was computed with the use of coefficients sharpened

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so that the average $|F_{hkl}|^2$ was independent of $\sin \theta$. The origin was partially removed. The coordinates of the sulfur atom were readily determined from the Harker vectors and it was quite easy to locate the rest of the atoms from a model of the Patterson function. The molecule is planar, except for the methylene hy-

drogens, and all of the sulfur to non-hydrogen vectors were located in the $(10\bar{2})$ plane.

A three-dimensional Fourier synthesis, computed with the signs determined from the model, confirmed the solution of the Patterson function. Four cycles of least-squares refinement using a CDC 3600 version of the Busing, Martin & Levy (1962) full-matrix program reduced the residual R_{F_2} ($R_{F_2} = \Sigma |F_o^2 - F_c^2| / \Sigma F_o^2$) to 0.28. Individual isotropic temperature factors as well as positional parameters were refined. The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$. The weighting scheme used was $w = 1/\sigma^2(F_o)^2$ for the observed reflections, while zero weights were assigned to the unobserved reflections. A three-dimensional difference Fourier computed after the fourth cycle indicated anisotropic movements of the atoms, and it was not possible to locate the hydrogen atoms with certainty. Anisotropic thermal parameters were introduced and two cycles of least-squares refinement reduced the residual R ($R = \Sigma |F_o - F_c| / \Sigma |F_o|$) to 0.102. At this stage the data were checked, a few misindexings were corrected and zero weights assigned to eight low-order reflections which were unreliable either because of extinction or because of very poor agreement in the original estimates. The four hydrogen atoms were then located in a difference Fourier. The peaks chosen ranged in height from 0.6 to 0.9 $e \cdot \text{\AA}^{-3}$ and made chemical sense. The contribution of the hydrogens was included in two cycles of anisotropic refinement. Finally the hydrogen parameters

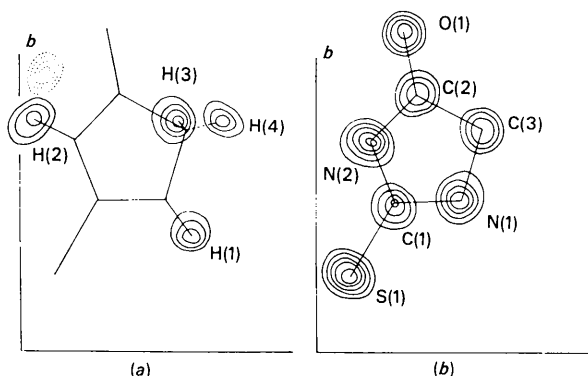


Fig. 1. (a) Composite map on $(10\bar{2})$ through the centers of the hydrogen atoms in the final difference map. Contours are at intervals of $0.25 e \cdot \text{\AA}^{-3}$, starting at $0.50 e \cdot \text{\AA}^{-3}$. A false maximum indicated by dotted contours lies very close to the $(10\bar{2})$ plane and should probably be interpreted as a residue from the oxygen atoms. (b) Section $(10\bar{2})$ of a final electron density map. Contours are at intervals of $2 e \cdot \text{\AA}^{-3}$, except for the sulfur atom where every other contour is omitted. The numbering system used in this paper is indicated.

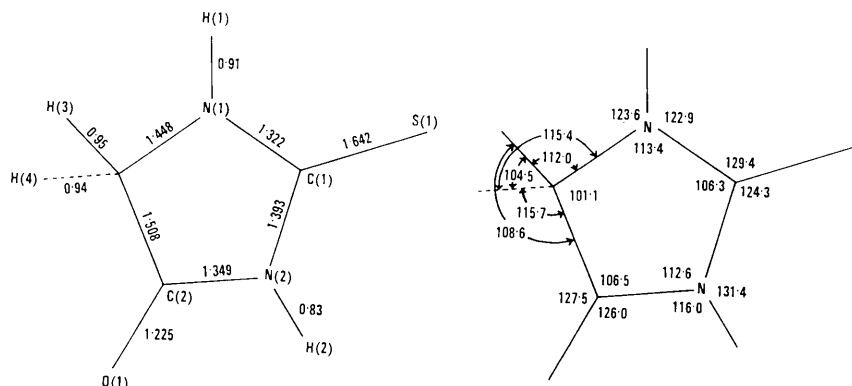


Fig. 2. Intramolecular bonds and angles in 2-thiohydantoin.

Table 1. Atomic coordinates and estimated standard deviations.

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
S(1)	0.0802	0.0001	0.1387	0.0001	0.0700	0.0001
C(1)	0.2369	0.0005	0.2568	0.0002	0.1304	0.0004
C(2)	0.3213	0.0004	0.4508	0.0002	0.1483	0.0003
C(3)	0.5258	0.0005	0.3875	0.0002	0.2638	0.0004
N(1)	0.4507	0.0004	0.2678	0.0002	0.2328	0.0004
N(2)	0.1625	0.0004	0.3688	0.0002	0.0767	0.0004
O(1)	0.3004	0.0003	0.5558	0.0002	0.1231	0.0003
H(1)	0.538	0.009	0.206	0.004	0.284	0.005
H(2)	0.041	0.008	0.393	0.004	0.009	0.005
H(3)	0.537	0.007	0.414	0.003	0.385	0.005
H(4)	0.679	0.008	0.401	0.004	0.234	0.006

Table 2. Thermal parameters

The anisotropic thermal parameters are converted from β_{ij} to the mean-square amplitude tensor U_{ij} . The expression for the temperature factor consistent with the U_{ij} values is:

$$\exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hka*b*U_{12} + 2hla*c*U_{13} + 2klb*c*U_{23})].$$

Table with 6 columns: S(1), C(1), C(2), C(3), N(1), N(2), O(1) and 6 columns of U values (U11, U22, U33, U12, U13, U23) multiplied by 10^3.

Standard deviations in U values are 0.001 Å^2 for all atoms. The isotropic B's for the four hydrogens were respectively 2.2 ± 0.8, 1.4 ± 0.6, 1.5 ± 0.7, and 3.1 ± 0.9.

Table 3. The observed and calculated structure factors

The three columns contain from left to right the values of I, 10 F_o and 10 F_c. 89 unobserved and 8 low order reflections, given zero weight in the refinements, are marked with an asterisk.

Large table with multiple columns containing reflection indices (h, k, l) and intensity values (I, 10 F_o, 10 F_c) for various reflections.

were refined isotropically. The final residual was 0.094. This value includes the contribution from eight low-order reflections and 89 unobserved reflections that were given zero weight in the least-squares refinements. In the final cycle of refinement the average shift of all parameters was 0.12 σ and the maximum shift was 0.48 σ [for β_{23} of N(1)]. The atomic scattering factors used were those given in *International Tables for X-ray Crystallography* (1962).

A final difference Fourier in which the hydrogens were not included in the structure factor calculation was computed [Fig 1(a)]. The enhancement of the hydrogen peaks in this final map indicated that the interpretation of the previous difference synthesis had been correct. The final Fourier is shown in Fig. 1(b) for comparison.

The final atomic parameters are given in Tables 1 and 2. The observed and calculated structure factors are listed in Table 3. The numbering system used is shown in Figs. 1(a) and (b).

Description of the structure

Bond distances and angles with their estimated standard deviations are given in Fig. 2 and Table 4.

The molecule is planar except for the methylene hydrogen atoms. Two least-squares planes were com-

Table 4. *Intramolecular bonds and angles*

	Distance	Standard Deviation ^a
S(1)-C(1)	1.642 Å	0.003
C(1)-N(2)	1.393	0.003
N(2)-C(2)	1.349	0.003
C(2)-O(1)	1.225	0.003
C(2)-C(3)	1.508	0.003
C(3)-N(1)	1.448	0.003
N(1)-C(1)	1.322	0.004
C(3)-H(3)	0.95	0.04
C(3)-H(4)	0.94	0.05
N(1)-H(1)	0.92	0.05
N(2)-H(2)	0.83	0.05

	Angle	Standard Deviation ^a
S(1)-C(1)-N(2)	124.3°	0.2°
C(1)-N(2)-C(2)	112.6	0.2
N(2)-C(2)-C(3)	106.5	0.2
N(2)-C(2)-O(1)	126.0	0.2
O(1)-C(2)-C(3)	127.5	0.2
C(2)-C(3)-N(1)	101.1	0.2
C(3)-N(1)-C(1)	113.4	0.2
N(1)-C(1)-N(2)	106.3	0.2
N(1)-C(1)-S(1)	129.4	0.2
C(1)-N(2)-H(2)	131.4°	2.8°
C(2)-N(2)-H(2)	116.0	2.8
C(3)-N(1)-H(1)	123.6	3.0
C(1)-N(1)-H(1)	122.9	3.0
H(3)-C(3)-H(4)	104.5	3.7
H(3)-C(3)-C(2)	108.6	2.5
H(3)-C(3)-N(1)	115.4	2.5
H(4)-C(3)-N(1)	112.0	3.1
H(4)-C(3)-C(2)	115.7	2.8

^a The standard deviations were estimated using the full variance-covariance matrix from the least-squares refinement.

puted by the method of Schomaker, Waser, Marsh & Bergman (1959). The data for the planes are given in Table 5. For the plane through the five atoms of the imidazolidine ring the average deviation is 0.01 Å, the maximum being 0.02 Å for atom N(1). The seven heavier atoms of the structure are coplanar within 0.03 Å, with an average deviation of 0.01 Å.

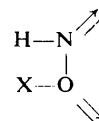
Table 5. *Least-squares planes*

The equation for the plane is $m_1x + m_2y + m_3z = d$, where x, y, z are fractional coordinates and d is the origin to plane distance in Å.

Plane through ring atoms			
$m_1 = -3.384$	$m_2 = 0.733$	$m_3 = 6.611$	$d = 0.2316$
		Deviation ($\times 10^2$ Å)	
N(1)			-2.20
N(2)			-0.41
C(1)			1.68
C(2)			-0.80
C(3)			1.72

Plane through the seven heavier atoms			
$m_1 = -3.3491$	$m_2 = 0.8785$	$m_3 = 6.6296$	$d = 0.3002$
		Deviation ($\times 10^2$ Å)	
S(1)			1.73
O(1)			-0.20
N(1)			-3.14
N(2)			-1.18
C(1)			-0.36
C(2)			0.32
C(3)			2.85

There are two main points of interest when discussing the structure of 2-thiohydantoin. The first one is the dimensions of the silver precipitating group



where X is S (Stephen & Townsend, 1965) The dimensions of this group are very similar to those found in rhodanine (van der Helm, Lessor & Merritt, 1962) as can be seen from Table 6. The two angles adjacent to the group are significantly different in the two compounds, but this must be attributed to the change in geometry of the ring system caused by the replacement of the ring sulfur-atom in rhodanine with an imino group. The other interesting point is the geometry of the heterocyclic ring itself. Recently the structure of DL-allantoin, also a derivative of hydantoin, was determined (Mootz, 1965) and a comparison of the bonds and angles in the two imidazolidine rings is given in Table 7. The shortening of the N(1)-C(1) bond, 1.322 Å in 2-thiohydantoin as compared to 1.341 Å in allantoin, can be expected from the presence of the thioketo group at C(1). The only other significant difference is

seen in the C–C bond involving the tetrahedral carbon in the ring. We find the value 1.508 Å, which is closer to the value of 1.501 Å proposed for a *sp*²–*sp*³ single carbon–carbon bond (*e.g.* Lide, 1962).

Table 6. Dimensions of the silver binding group

	Rhodanine	2-Thiohydantoin
S–C	1.64 Å	1.642 Å
C–N	1.37	1.393
<NCS	124.2°	124.3°
<CN⇌	116.8	112.6
<NC→	111.8	106.3

Table 7. The geometry of the imidazolidine ring

Bond*	DL-Allantoin	2-Thiohydantoin
N(1)–C(1)	1.341 Å	1.322 Å
C(1)–N(2)	1.397	1.393
N(2)–C(2)	1.362	1.349
C(2)–C(3)	1.535	1.508
C(3)–N(1)	1.461	1.448

Angle	DL-Allantoin	2-Thiohydantoin
N(1)–C(1)–N(2)	107.7°	106.3°
C(1)–N(2)–C(3)	111.6	112.6
N(2)–C(2)–C(3)	106.9	106.5
C(2)–C(3)–N(1)	100.7	101.1
C(3)–N(1)–C(1)	112.7	113.4

* The labelling of the atoms refers to the diagram above.

The molecular packing in one of the infinite sheets parallel to (10 $\bar{2}$) is shown in Fig. 3. Hydrogen bonds of the type N–H...O link the molecules together, each oxygen accepting two hydrogen bonds, one from the N(1) of one molecule and the other from the N(2) of another. Details concerning the hydrogen bonds are given in Table 8. Two N(2)–H...O(1) bonds of length 2.916 Å are formed between pairs of molecules related by a center of symmetry, while the N(1)–H...O(1) bonds of length 2.928 Å between molecules related to each other by the two-fold screw axes complete the two-dimensional network of molecules.

Table 8. Geometry of the hydrogen bonds

N in basic molecule	N(1)H...O(1)	N(2)H...O(1)
O in molecule at	(1-x, -½+y, ½-z)	(x̄, 1-y, z̄)
d(N–H)	0.91 Å	0.83 Å
d(H...O)	2.02	2.10
d(N...O)	2.928	2.916
<(N–H...O)	173°	170°

The hydrogen bonded sheets are held together by weak van der Waals forces. The interplanar spacing *d*_{10 $\bar{2}$} is 3.2 Å but no intermolecular distances shorter than 3.3 Å were found. The closest intermolecular distance between heavy atoms not in the same plane is 3.396 Å, between N(1) in the basic molecule and C(1) in the molecule related by (x, ½-y, ½+z).

The sulfur atoms related by the center of symmetry at (0,0,0) are 3.432 Å apart. This again verifies earlier findings [*e.g.* Marsh (1955), Donohue (1950), van der Helm, Lessor & Merritt (1962)] that the van der Waals radius of sulfur is closer to 1.72–1.73 Å than to the value of 1.85 Å given by Pauling (1960).

The closest intermolecular non-hydrogen bonded contacts in the plane, apart from S–S, are 3.65 Å for C(3) in the basic molecule to S(1) of the molecule related by (1+x, ½-y, ½+z), and 3.73 Å for C(3) in the basic molecule to S(1) of the molecule related by (1-x, ½+y, ½-z).

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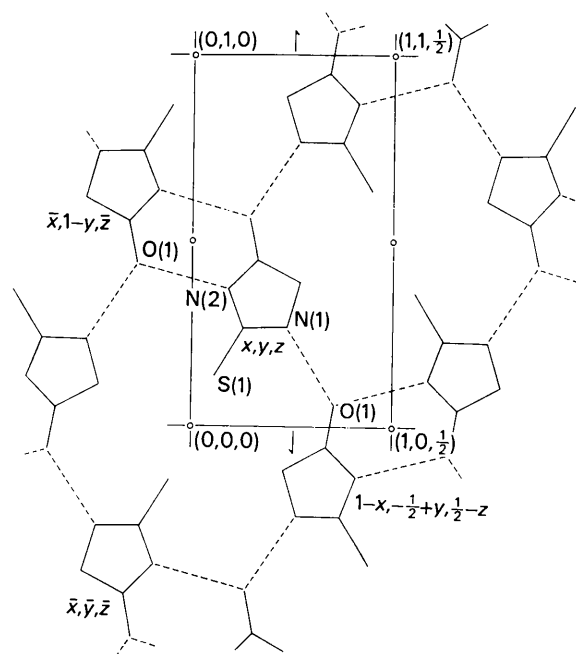


Fig. 3. The molecular packing in one of the infinite sheets parallel to (10 $\bar{2}$). Hydrogen bonds are indicated by the hydrogen atoms have been omitted.

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The Crystal and Molecular Structure of Hydrazinium Hydrazinedithiocarboxylate

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The crystal structure of hydrazinium hydrazinedithiocarboxylate, $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NH-CSS})$, has been solved by a new method of sign determination and refined three-dimensionally by differential syntheses. The hydrazinedithiocarboxylate anions form layers parallel to (010) and the hydrazinium cations form hydrogen bonds between one another, normal to (010). The $\text{N}'\text{-N-CSS}$ group, which can be considered as a dithiocarbamate anion, is planar; the main interatomic distances in the anion are: C-S 1.723 and 1.695 Å, C-N 1.330 Å and $\text{N}'\text{-N}$ 1.414 Å. The distance between nitrogen atoms in the hydrazinium cations is 1.436 Å. The whole structure is held together by a network of hydrogen bonds.

Introduction

The study of the crystal structure of hydrazinium hydrazinedithiocarboxylate, $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NH-CSS})$, has been undertaken as an extension of the studies on crystal and molecular structures of salts of hydrazine-carboxylic acid. Hydrazinedithiocarboxylic acid can be considered also as a derivative of dithiocarbamic acid and interesting comparisons can be made with the structures of dithiocarbamates.

Experimental

The compound was prepared by reaction of hydrazine hydrate and carbon sulphide (Curtius & Heidenreich, 1894). The material was recrystallized from water. The crystals obtained were colorless, well formed, fairly unstable prisms. Their composition was confirmed by chemical analysis.

Crystal data

Compound: hydrazinium hydrazinedithiocarboxylate
 $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NH-CSS})$
F.W. 140.24.

Crystal habit: prisms, elongated along [010].

Crystal class: monoclinic, prismatic.

Unit cell: from rotation and Weissenberg photographs around [100] and [010] (Cu $K\alpha$, $\lambda = 1.5418$ Å)
 $a = 7.108(6)$, $b = 6.828(3)$, $c = 11.993(7)$ Å
 $\beta = 90.65(15)^\circ$
 $V = 582.0$ Å³ $Z = 4$
 $D_m = 1.599$ (by flotation), $D_x = 1.600$ g.cm⁻³
 $\mu(\text{Cu } K\alpha) = 70.67$ cm⁻¹.

Space group: $P2_1/c$ (C_{2h}^5 , no. 14), from systematic absences.

Intensity measurements

Integrated reflexions $h0l$, ... $h5l$ and $0kl$, ... $4kl$, obtained by a Weissenberg camera, were measured by a microdensitometer. Absorption corrections were applied as for cylindrical specimens ($\mu\bar{R} = 0.85$).

The structure factor and refinement calculations were performed on the computer Olivetti Elea 6001/S of the Centro Elettronico of the University of Parma. The calculations related to the application of the direct method for sign determination were carried out at the computing centre of the Polytechnic of Milan, on a IBM-7040 computer.