

Crystal Structure of 3-Hydrazino-5-thiol-1,2,4-triazole*

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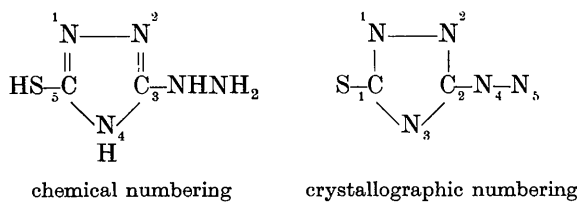
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According to single crystal X-ray diffraction data 3-hydrazino-5-thiol-1,2,4-triazole is monoclinic, space group $P2_1/c$, with $a = 4.76 \pm 0.01$, $b = 15.61 \pm 0.02$, $c = 7.35 \pm 0.02$ Å, and $\beta = 108^\circ 35' \pm 5'$. The atomic positions were determined by Fourier and least-squares methods using three-dimensional data. The molecules are planar except for the terminal N of the hydrazino group. Hydrogen bonds of length 2.88 ± 0.01 Å between nitrogens adjacent to hydrazino carbons link the rings into nearly flat ribbons. It is suggested that the proton of the thiol is transferred to the terminal N of the side chain resulting in ionic bonding between adjacent ribbons with S-N = 3.24 Å. Bond distances in Å within the molecule are (each ± 0.01 Å): C-S = 1.74; N-N = 1.40 (ring), 1.40 (side chain); C-N = 1.37 (side chain), 1.32, 1.37, 1.35, 1.28 (around ring in sequence N, C (hydrazino), N, C (thiol), N).

Introduction

Compounds containing unsaturated rings of carbon and nitrogen atoms provide interesting examples of the effect of electronic structure on bond distances. The compound considered in this paper was chosen, on the basis of crystallographic suitability, from among several such heterocyclic compounds generously provided us by Dr Earl S. Scott.

Arndt & Bielich (1923) isolated a compound $C_2H_5N_5S$ from a mixture prepared by refluxing hydrazodicarbothiamide in hydrazine. It was shown to be 3-hydrazino-5-thiol-1,2,4-triazole by Fromm & Wettarik (1926) and by Hoggarth (1952). The structure can be represented as:



However, the chemical evidence does not establish the location of the hydrogen atom on the ring, nor are the double bonds to be considered localized.

Crystallographic data

The crystals were prepared by recrystallization of a sample received from Dr Scott. The crystals melt at 240 °C. (Scott & Audrieth, 1954). They are small thin plates having the b axis normal to the plane of the plate. Optical extinctions are found approximately

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parallel and perpendicular to the $(10\bar{2})$ plane, with the slow ray parallel to the $(10\bar{2})$ plane.

The unit-cell dimensions were derived from Weissenberg photographs calibrated with a thin quartz fiber ($a = 4.913$ Å) and a precession photograph (for determination of β):

$$a = 4.76 \pm 0.01, \quad b = 15.61 \pm 0.02, \quad c = 7.35 \pm 0.02 \text{ Å}; \\ \beta = 108^\circ 35' \pm 5'.$$

The systematic absences, ($h0l$ absent if l is odd, $0k0$ absent if k is odd) suggest space group $P2_1/c$, and this assignment is confirmed by the structure determination. The density measured approximately by flotation of very small crystals corresponds to 4.06 molecules per unit cell.

Intensity data were obtained from multiple-film Weissenberg photographs (Cu $K\alpha$ radiation) by visual comparison with a set of standard spots. Layers zero through four about the c axis and zero through three about the a axis yielded 908 independent reflections, including 200 too weak to be observed. These constitute approximately 80 per cent of the data available in the copper sphere of reflection.

Determination of the structure

The assumption that all atoms are in general positions of the space group $P2_1/c$

$$4(e): \quad \pm(x, y, z; x, \frac{1}{2}-y, \frac{1}{2}+z)$$

was justified by the subsequent results. The Harker sections $P(x, \frac{1}{2}, z)$ and $P(0, y, \frac{1}{2})$, though poorly resolved, gave an approximate location for the sulfur atom. Signs were calculated for sulfur (at $y = 0.055$, $z = 0.25$) for half of the terms for the electron-density projection $\rho(y, z)$. From this incomplete projection it was possible to pick out a ring system more or less parallel to $(10\bar{2})$, in agreement with the optical bi-

Table 1. *Final atomic parameters and isotropic temperature factors*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
S	0.3213 ± 0.0006	0.0551 ± 0.0002	0.2328 ± 0.0004	2.2
C ₁	0.104 ± 0.002	0.1435 ± 0.0005	0.134 ± 0.001	1.5
C ₂	-0.056 ± 0.002	0.2732 ± 0.0006	0.070 ± 0.001	1.9
N ₁	-0.154 ± 0.002	0.1423 ± 0.0005	0.008 ± 0.001	2.1
N ₂	-0.268 ± 0.002	0.2246 ± 0.0006	-0.041 ± 0.001	2.4
N ₃	0.179 ± 0.002	0.2260 ± 0.0005	0.179 ± 0.001	1.6
N ₄	-0.074 ± 0.002	0.3605 ± 0.0006	0.078 ± 0.001	2.3
N ₅	0.191 ± 0.002	0.4028 ± 0.0006	0.175 ± 0.001	2.5

refringence, which gave a satisfactory packing of the molecules. This projection was refined by four Fourier calculations and by four cycles of least-squares. The final projection resolved all eight atoms other than hydrogen.

It was deduced that a projection along [101] would also resolve the molecule. A trial structure based on the assumption that the molecule is parallel to (10 $\bar{2}$) was refined by least-squares using the *hkh* data. The position of N₅, which was incorrectly placed, was determined by a Fourier projection, and the refinement was continued by least-squares. The final projection resolved six atoms, though not as well as in the previous case. Atoms C₁ and N₂ were not resolved.

The parameters from these two-dimensional refinements were refined by five cycles of least-squares using the three-dimensional data. The final coordinates, their standard deviations, and the individual isotropic temperature factors are listed in Table 1.

The least-squares refinements were made with an I.B.M. 650 computer with a program, referred to as 'Least-Squares I', which was written for crystal class 2/*m*. The same program was used in the final refinement of the structure of gold chloride (Clark, Templeton & MacGillavry, 1958). Some details of the program were modified as the work proceeded. Subsequently a major revision was made to extend the calculation to non-centric space groups and to increase the convenience of use. In this revised form it is now known as 'Least-Squares II' (Senko, 1957).

At each cycle of the least-squares refinement three 'unreliability factors' were calculated. In order to prevent bias in the scale factors, each *F_o*, for an unobserved reflection, was set equal to the average *F_c* for unobserved reflections from the previous cycle. The final values were:

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.184,$$

$$R_2 = \frac{(\sum (|F_o| - |F_c|)^2 / \sum F_o^2)^{1/2}}{\sum F_o^2} = 0.212,$$

$$R_3 = \frac{(\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}}{\sum w F_o^2} = 0.218.$$

The value of *R*₁ is 0.158 with the omission of unobserved reflections and also the two strongest reflections, (10 $\bar{2}$) and (11 $\bar{2}$), which may suffer from extinction. *R*₃ is the function which is minimized by the least-squares refinement. The weights *w* were taken, in the final refinements, as the lesser of (4*F*_{min})⁻² or *F*_o⁻², according to Hughes (1941).

A synthesis of *F_o* - *F_c*, projected along [100], Fig. 1,

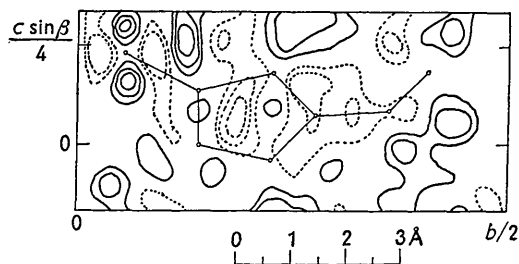


Fig. 1. Synthesis of *F_o* - *F_c*, projected along *a*. Contours are at intervals of 0.5 e.Å⁻². The zero contour is omitted. Negative contours are dotted.

suggests considerable anisotropy of the vibrations of the sulfur atom. However, all calculations were made with the assumption of isotropic vibrations since it did not seem feasible with our equipment to consider

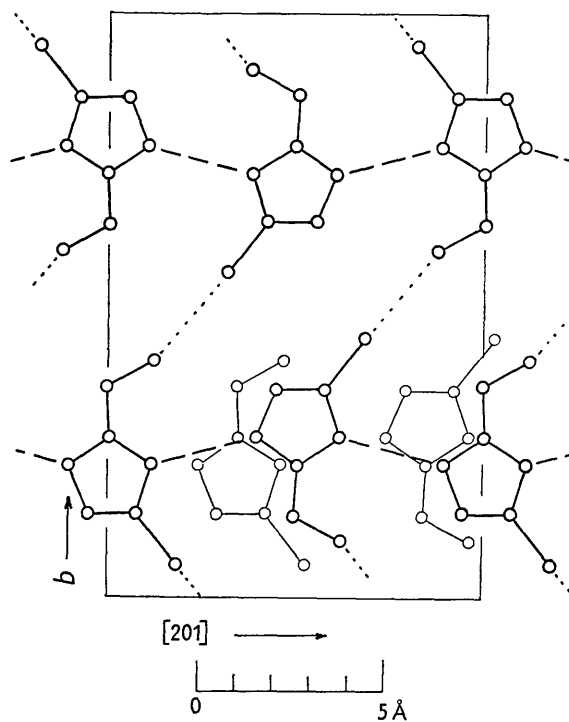


Fig. 2. The crystal structure viewed perpendicular to (10 $\bar{2}$). Dashed lines indicate hydrogen bonds. The dotted lines indicate the 3.24 Å distance between S and N₅ of adjacent chains. The rectangle indicates unit translations in the *b* and [201] directions. Two molecules of the next layer are indicated by lighter lines.

the anisotropy. Hydrogen atoms also were excluded from the structure factor calculations.

Discussion of the structure

Nearly planar molecules are linked by hydrogen bonds into flat chains, or ribbons, running parallel to [201], as shown in Fig. 2. The molecules are tilted only about 3° from positions parallel to (10 $\bar{2}$). The ribbons are stacked with longitudinal displacement on top of ribbons of the same polarity with respect to the chain direction. Ribbons of opposite polarity alternate in the *b* direction.

A plane was fitted by least-squares to the five atoms in the ring. The distances of the atoms from this plane are listed in Table 2. The primed atom occurs in the

Table 2. Distances of atoms from least-squares plane through the ring

S	0.009 Å	N ₁	0.002 Å	N ₄	0.055 Å
C ₁	0.000	N ₂	-0.005	N ₅	-0.194
C ₂	0.006	N ₃	-0.004	N ₂	0.023

adjacent molecule in the chain. Since the standard deviation of position is about 0.003 Å for sulfur and 0.009 Å for the other atoms, the ring is planar well within the experimental error. Only N₅, the terminal atom of the side chain, is significantly outside the plane of the ring, and the deviation of N₄ is of doubtful significance.

The bond distances and angles are given in Fig. 3 and Fig. 4. The standard deviations are about 0.010 Å for the S-C bond, 0.015 Å for the hydrogen bond, 0.013 Å for the other bonds, and 0.7° for the angles. All the bonds observed in the molecule are intermediate

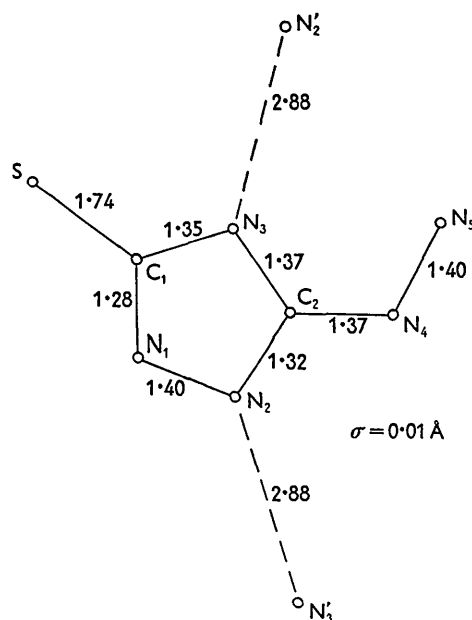


Fig. 3. Bond distances in Å.

between the distances expected for pure single and double bonds: 1.47 and 1.26 Å for C-N bonds (Donohue, Lavine & Rollett, 1956), 1.47 and 1.24 Å for N-N bonds (Bryden, 1958), and 1.79 and 1.60 Å for C-S bonds (Cox, Gillot & Jeffrey, 1949). Attempts to explain the distances in a simple and plausible way by writing resonance forms have failed. Particularly unpleasing structures are required to introduce double-bond character into the N-N bond of the side chain. However, somewhat similar bonds have been

Table 3. Observed and calculated structure factors

The data are grouped according to the value of *h*. In each set of four columns *k*, *l*, *F_o*, and *F_c* (followed by its sign if negative) are listed in order. After completion of the calculations it was discovered that three errors had been made in the data used in the least-squares refinement and in the calculation of *R*₁, *R*₂, and *R*₃: 18, 57, and 19 were used rather than 0, 0, and 62 for *F_o* for (551), (333), and (430). Correction of these errors reduces the value of *R*₁ by 0.003 and is expected to have a negligible effect on the structure.

h = 0															
2 0 59 82-	18 1 9 3-	8 3 11 6-	17 4 21 20-	10 6 23 29											
4 0 37 34-	0 2 32 28-	9 3 21 22	1 5 35 40	11 6 11 8											
6 0 111 88-	1 2 117 150-	10 3 21 20	2 5 0 10-	12 6 17 16											
8 0 28 21	2 2 125 144-	11 3 36 34	3 5 17 17-	13 6 11 10											
10 0 120 104-	3 2 56 54-	12 3 67 68-	4 5 76 89-	1 7 0 5-											
12 0 60 51-	4 2 43 31-	13 3 0 6-	5 5 21 20	2 7 21 24											
14 0 69 60	5 2 12 15	14 3 29 24-	6 5 19 20-	3 7 35 43-											
16 0 0 11-	6 2 76 73	15 3 11 7-	7 5 19 18-	4 7 29 33											
18 0 37 28	7 2 28 30	16 3 34 29-	8 5 26 24-	5 7 0 3											
20 0 15 13	8 2 92 98	17 3 22 16-	9 5 11 8-	6 7 17 18											
1 1 17 24	9 2 36 35-	0 4 62 59	10 5 33 49	7 7 28 38											
2 1 45 51-	10 2 31 21	1 4 36 36	11 5 44 54-	8 7 0 1											
3 1 36 41-	11 2 18 13	2 4 42 46	12 5 16 16-	9 7 18 21											
4 1 62 67-	12 2 18 11	3 4 16 12	13 5 19 17	10 7 8 10-											
5 1 42 40	13 2 32 26	4 4 22 24	14 5 37 37	11 7 12 14-											
6 1 86 108-	14 2 27 22	5 4 56 67	15 5 9 8	12 7 8 6-											
7 1 0 0	15 2 37 17-	6 4 27 27-	16 5 12 13	0 8 0 2											
8 1 52 52-	16 2 38 26-	7 4 0 6-	0 6 15 17-	1 8 0 9											
9 1 0 6-	17 2 0 7	8 4 49 52-	1 6 0 7-	2 8 25 29											
10 1 13 10	18 2 40 32-	9 4 23 23-	2 6 28 30	3 8 0 8											
11 1 47 38-	1 3 0 6	10 4 42 42-	3 6 23 27-	4 8 15 18-											
12 1 81 72	2 3 78 83	11 4 0 2-	4 6 19 17-	5 8 19 25											
13 1 21 17	3 3 22 24-	12 4 23 22-	5 6 31 33-	6 8 12 15											
14 1 61 47	4 3 42 40	13 4 0 3-	6 6 11 9	7 8 11 13											
15 1 0 7	5 3 38 38-	14 4 11 3	7 6 15 12-	8 8 11 16-											
16 1 31 20	6 3 82 91	15 4 9 6-	8 6 31 32												
17 1 0 3-	7 3 23 23	16 4 23 21	9 6 0 6												
h = 1															
0 0 111 154	9 1 37 30	16 2 28 21	6 4 0 11-	3 6 47 46											
1 0 18 15-	10 1 15 5-	17 2 25 18-	7 4 42 42-	4 6 25 26-											
2 0 92 116-	11 1 106 93	18 2 0 6-	8 4 0 7	5 6 15 14											
3 0 119 133-	12 1 15 4-	1 3 61 59	9 4 0 1-	6 6 19 20											
4 0 66 70-	13 1 19 16-	2 3 37 34	10 4 0 7	7 6 40 41											
5 0 122 114-	14 1 12 8-	3 3 76 71	11 4 26 24	8 6 0 6											
6 0 37 28	15 1 17 10-	4 3 80 76-	12 4 0 3	9 6 8 8											
7 0 40 30	16 1 12 11-	5 3 39 36	13 4 44 34	10 6 0 2-											
8 0 97 67	17 1 49 39-	6 3 16 15	14 4 0 3-	11 6 26 24-											
9 0 43 35	18 1 0 4-	7 3 39 36-	15 4 39 33	12 6 7 6											
10 0 9 9-	19 1 17 12-	8 3 0 5-	1 5 47 47-	13 6 24 26-											
11 0 36 25	0 2 24 15-	9 3 76 75-	2 5 44 44	1 7 43 49											
12 0 0 0	1 2 68 53	10 3 49 55	3 5 42 42-	2 7 12 13											
13 0 29 18	2 2 25 30	11 3 0 3-	4 5 23 20-	3 7 0 5-											
14 0 34 31	3 2 70 58	12 3 58 54-	5 5 19 17	4 7 12 12											
15 0 51 36	4 2 29 27-	13 3 30 30-	6 5 26 28-	5 7 21 24-											
16 0 31 26-	5 2 106 102	14 3 17 16	7 5 53 51	6 7 0 0											
17 0 25 19	6 2 52 44	15 3 24 18	8 5 10 11	7 7 0 8											
18 0 28 20-	7 2 34 34	16 3 0 4	9 5 33 33	8 7 0 5											
1 1 89 98-	8 2 8 7-	17 3 31 23	10 5 16 20	9 7 28 30-											
2 1 64 62	9 2 0 9-	18 3 7 11	11 5 0 3	0 8 12 12-											
3 1 7 9-	102 48 42-	0 4 23 23	12 5 22 23-	1 8 0 5-											
4 1 60 47	11 2 35 26-	1 4 0 2-	13 5 17 16	2 8 21 23											
5 1 58 52-	12 2 15 14-	2 4 0 2	14 5 7 7	3 8 12 17-											
6 1 26 16	13 2 47 38-	3 4 15 44-	0 6 22 16-	4 8 9 13-											
7 1 86 86	14 2 15 10	4 4 16 14-	1 6 9 10-	5 8 12 17-											
8 1 16 16-	15 2 37 28-	5 4 67 62-	2 6 8 9												

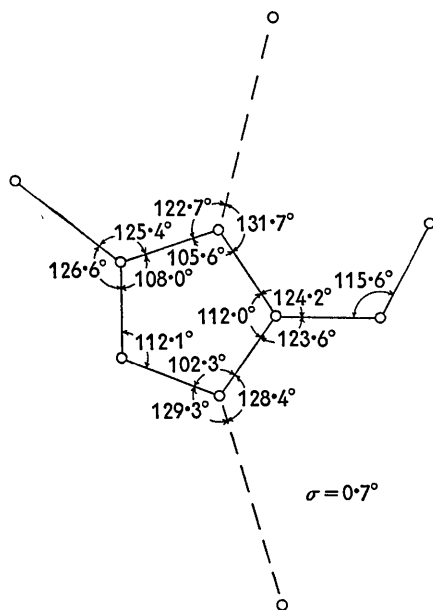
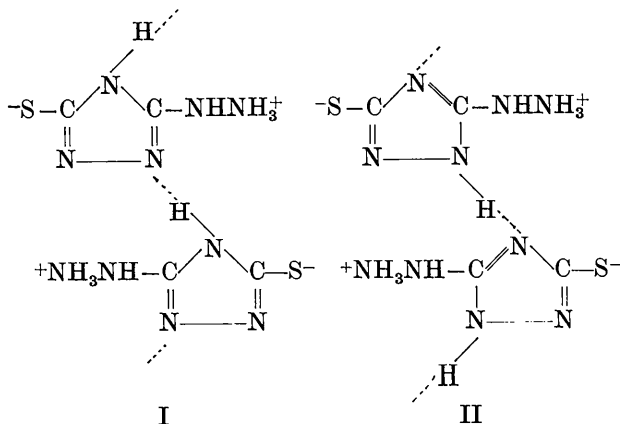


Fig. 4. Bond angles.

observed as 1.42 Å in $N_2H_6Cl_2$ (Donohue & Lipscomb, 1947) and 1.43 Å in the 5-aminotetrazole salt of hydrazine (Bryden, 1958). Our value is lower than these only by 2 or 3 standard deviations.

The shortest intermolecular distance is the hydrogen bond between N_3 and N'_2 , 2.88 Å. This distance is one of the shortest which has been reported for an $N-H \cdots N$ bond. The location of the hydrogen in this bond is uncertain because there are two possible tautomeric structures:



The bond angles at each end of the hydrogen bond are reasonable, and the bond is in the plane of one ring and within about 1.5° of the plane of the other ring. The fact that the C_2-N_2 bond is slightly shorter than the C_2-N_3 bond tends to make tautomer I, with hydrogen on N_3 , more likely. Disorder of the hydrogen position is also possible.

The next shortest intermolecular N-N distance (3.30 Å) is between atoms N_1 and N_4 . A hydrogen bond is not plausible in this instance because of the rather long distance and because it would require an unusually small bond angle, $\angle N_5-N_4-N'_1 = 83^\circ$. All other intermolecular N-N distances exceed 3.36 Å.

The sulfur atom has several nitrogen neighbors. The nearest is N_5 at a distance of 3.24 Å, indicated by the dotted lines in Fig. 2. In this case the bond angles, $\angle C_1-S-N'_5 = 163^\circ$ and $\angle N'_4-N'_5-S = 155^\circ$, are poor for hydrogen bonding. The close proximity of these atoms suggests ionic bonding which ties the ribbons together in sheets. For this reason the tautomers above are written as zwitterions. The next shortest intermolecular S-N distances are 3.44 Å to N_4 , 3.52 Å to N_1 , and 3.56 and 3.62 Å to other N_5 atoms.

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