

# The Crystal and Molecular Structure of Benzaldehyde Thiosemicarbazone

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Benzaldehyde thiosemicarbazone forms rectangular plate-like orthorhombic crystals elongated parallel to *b*-axis with unit cell dimensions of *a* = 20.989(5), *b* = 6.186(1), *c* = 7.659(2) Å. The space group is  $P2_12_12_1$  and there are four molecules per unit cell, *D<sub>m</sub>* is 1.18(2) g cm<sup>-3</sup> and *D<sub>c</sub>* is 1.16 g cm<sup>-3</sup>. The structure has been solved by direct methods and refined by least-squares to an *R* index of 0.05 for 1125 observed reflections with a diffractometer. The structure comprises one molecule per asymmetric unit. The benzene ring and the thiosemicarbazide group are individually planar, but the thiosemicarbazide group is tilted by ~11° to the mean benzene plane. The C–S bond distance 1.686 Å is similar to that found in other thiosemicarbazones. The N–N bond length of 1.389 Å is interpreted in terms of the conjugation of the side-chain with the benzene ring.

Thiosemicarbazones have attracted special attention on account of their biological activities<sup>1</sup>. The biological activity of these compounds has been suggested to be enhanced considerably by binding with trace metals<sup>2</sup>. All tumor inhibitors are potentially capable of acting as tridentate N–N–S type<sup>3–5</sup> or O–N–S type<sup>6–8</sup> ligands. Benzaldehyde thiosemicarbazone (BZTSC) is devoid of any biological activity and can function only as a bidentate ligand<sup>9</sup>. Therefore, the desire for a comparison of the molecular geometries and stereochemistries of the two types of compounds, active and inactive, prompted us to undertake the X-ray structure analysis of the title compound.

## Results and Discussion

Since there is one molecule in the asymmetric unit for four molecules per unit cell of the space group  $P2_12_12_1$ , it required the determination of the dimensions of one molecule of BZTSC. The atomic numbering scheme, bond distances and interbond angles in the BZTSC molecule are given in Fig. 1. Projection of the contents of the unit cell, except the H atoms, is shown in Fig. 2. The diagram depicts the packing arrangement and orientation of the molecules and the atomic numbering scheme adopted in the description of the molecular structure. From Fig. 2 it is evident that the structure consists of discrete BZTSC molecules which are linked by van der Waals forces. The C–S bond distance of 1.686(4) Å is shorter than the usual single bond distance of 1.82 Å and larger than the C–S double bond of 1.56 Å, quoted by Sutton<sup>10</sup>, due to the conjugation of the system. The C(2)–N(1) bond of 1.28 Å should be a double bond<sup>6</sup>. The bond distances C(1)–N(3), 1.321(6), and C(1)–N(2), 1.343(5) Å are considerably shorter than a C(*sp*<sup>2</sup>)–N bond, 1.446 Å, as calculated from the sum of the covalent radii of C(*sp*<sup>2</sup>) and N<sup>11</sup>. Consequently, these bonds are indicative of only partial double bond character<sup>5,6,9</sup>. The slight difference in the two values is reasonable because the N(3) atom forms a part of an NH<sub>2</sub> group, while the N(2) atom forms a part of an NH group. The bond dis-

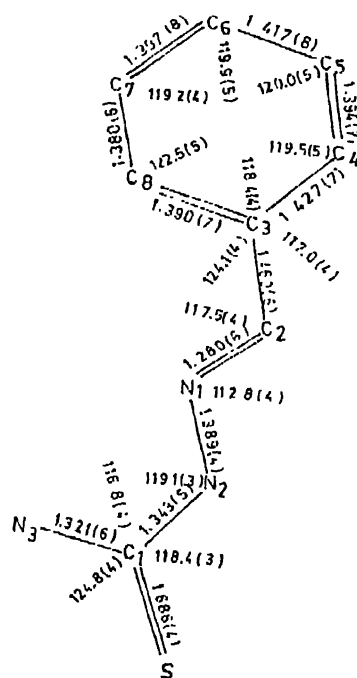


Fig. 1. Bond lengths (Å) and interbond angles (°) for benzaldehyde thiosemicarbazone; estimated standard deviations are given in parenthesis.

tance N(1)–N(2), 1.389 Å, is in agreement with the value found in related thiosemicarbazones<sup>6</sup> and is considerably less than the accepted N–N bond length of 1.44 Å. The bond-length C(2)–C(3), 1.460 Å, is shorter than a typical C–C bond 1.54 Å. Similar behaviour has been noticed in 2FFTSC<sup>7</sup>, 2FTTSC<sup>12</sup>, 4FPYTSC<sup>5</sup>, furildioxime<sup>13</sup>, *trans*-β-2-furylacrylic acid<sup>14</sup> and furoic acid<sup>15</sup>. The shorter bond distances point to extensive conjugation between the thiosemicarbazide side-chain and the aromatic ring. This conjugation would not be possible if the C(3) atom were a part of the linear chain or a saturated ring system<sup>9,16</sup>.

<sup>†</sup>Since deceased.

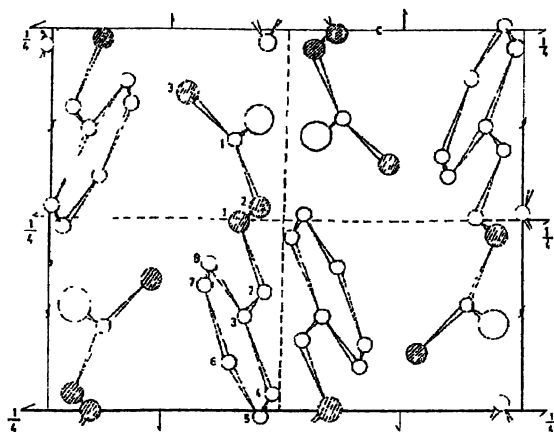


Fig. 2. Unit cell contents of benzaldehyde thiosemicarbazone projected on 100 plane; numbering scheme of atoms is shown for one molecule.

The mean value of bond lengths in the benzene ring is  $1.40 \text{ \AA}$  as expected though there is a variation in the individual bond lengths. The internal angles of the benzene ring also show variation with the minimum value  $118.4^\circ$  for C(4)–C(3)–C(8) and the maximum value  $122.5^\circ$  for C(3)–C(8)–C(7). However, the average value  $119.9^\circ$  of interbond angles of the ring is the ideal one. Though the two parts of the molecule, viz. the benzene ring and the thiosemicarbazide group are individually planar, the same is not true for the molecule as a whole. In the thiosemicarbazide moiety, the C(2) atom points up ( $+0.04 \text{ \AA}$ ) and the N(1) atom points down ( $-0.04 \text{ \AA}$ ) from the best thiosemicarbazide plane. The thiosemicarbazide group is tilted to the benzene ring by  $\sim 11^\circ$  and this tilt is similar to the value found in 4-formylpyridine thiosemicarbazone<sup>5</sup> where the thiosemicarbazide group is tilted by  $\sim 14^\circ$  to the mean pyridine plane.

The C–S bonds are *trans* to the N–N bonds and the same conformation has been found in 2FFTSC<sup>7</sup>, 4FPYTSC<sup>5</sup>, 2FTTSC<sup>12</sup> and thiosemicarbazide<sup>17</sup>. In the formation of metal complexes, N(1) and S must adopt a *cis*-conformation. A change in conformation about the C(1)–N(2) bond which possesses a considerable double bond character will occur in the metal complex formation which would require a  $180^\circ$  rotation about this bond. The title compound, BZTSC, is inactive, probably due to the absence of any planar N–N–S or O–N–S type ligand, which is an essential requirement for thiosemicarbazones to exhibit biological activity.

## Experimental

Benzaldehyde thiosemicarbazone (BZTSC) was prepared by the standard method<sup>18</sup> and crystallised from ethanol. Recrystallisation was carried out several times to get

pure rectangular plate-like crystals elongated parallel to *b*-axis. Oscillation and Weissenberg photographs showed the crystal to be orthorhombic. The systematic absences,  $h00$  for  $h = 2n + 1$ ,  $0k0$  for  $k = 2n + 1$ , and  $00l$  for  $l = 2n + 1$ , indicated the space group to be  $P2_12_12_1$ .

A thin rectangular crystal ( $0.30 \times 0.31 \times 0.13 \text{ mm}$ ) was mounted with *b*-axis parallel to  $\phi$ -axis of the diffractometer and then used for the measurement of intensities. The cell constants determined from the oscillation and Weissenberg photographs were refined by the least-squares method from the  $2\theta$  values of 15 reflections measured on the diffractometer. The values of the unit cell parameters with their estimated standard deviations are  $a = 20.989(5)$ ,  $b = 6.186(1)$ ,  $c = 7.659(2) \text{ \AA}$  and  $V = 994.4 \text{ \AA}^3$ . The density calculated for four molecules of  $C_8H_9N_3S$ , molecular weight 179, per unit cell is  $1.16 \text{ g cm}^{-3}$ , in good agreement with the value  $1.18(2) \text{ g cm}^{-3}$  measured by floatation in a mixture of *m*-xylene and bromoform.

Intensity data were measured with a TDC-312 diffractometer using zirconium filtered  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Intensity of each reflection was recorded by  $2\theta$ - $\omega$  step scan technique with a scan width of  $1.5^\circ$  divided into 51 steps and having 10 steps of background on each side of the scan. A set of four standard reflections were measured after every 100 reflections and showed only a slight variation (maximum 1%) over the period of intensity measurements. A total of 1406 unique reflections with  $2\theta \leq 55^\circ$  were estimated. The 1125 (80%) reflections that were greater than 1.20 times the background were considered to be observed and were used in the structure analysis. The intensities were reduced to a set of structure amplitudes on an arbitrary scale by application of the Lorentz-polarisation corrections. No absorption correction was applied.

**Structure determination and refinement:** The structure was solved by the direct phasing multisolution program MULTAN 80 of Main<sup>19</sup>, using 198 reflections with  $E > 1.3$ . The highest peak in the *E*-map was assigned to the S-atom and the other non-hydrogen atoms were located from a series of weighted Fourier syntheses using MULTAN 80. The structure factors calculated using all non-hydrogen atoms gave an *R* index of 0.39. The structure was refined by full-matrix least-squares initially using isotropic thermal parameters and then anisotropic thermal parameters, to an *R* index of 0.05. Unit weights were used throughout the refinement. As the positions of the hydrogen atoms were not clearly indicated in the final differences Fourier map, no attempt was made to locate these atoms. The scattering factors for all the atoms were taken from the International Tables for X-ray Crystallography<sup>20</sup> and all the calculations were carried out on a DEC-20 computer. The final positional parameters of the non-hydrogen atoms and their equivalent isotropic thermal parameters are given in Table 1.

The bond lengths and the interbond angles are shown in Table 2.

TABLE 1—FINAL POSITIONAL PARAMETERS OF NON-HYDROGEN ATOMS AND THEIR EQUIVALENT ISOTROPIC THERMAL PARAMETERS

$$B_{eq} = 4/3[B_{11}/a^{*2} + B_{22}/b^{*2} + B_{33}/c^{*2}]$$

Atom	X	Y	Z	$B_{eq}$ (Å <sup>2</sup> )
S	0.4756(1)	0.2262(2)	0.4398(2)	3.76(2)
N(1)	0.6422(1)	0.5021(6)	0.4028(4)	3.45(5)
N(2)	0.5792(1)	0.4582(6)	0.4463(4)	3.45(6)
N(3)	0.5868(2)	0.1552(7)	0.2808(6)	4.87(8)
C(1)	0.5518(2)	0.2777(7)	0.3844(6)	3.68(7)
C(2)	0.6611(2)	0.6857(9)	0.4597(7)	4.87(10)
C(3)	0.7263(2)	0.7508(8)	0.4184(5)	3.78(7)
C(4)	0.7468(2)	0.9564(8)	0.4816(6)	4.34(9)
C(5)	0.8097(3)	1.0207(9)	0.4562(7)	5.48(10)
C(6)	0.8547(2)	0.8737(11)	0.3857(6)	5.26(12)
C(7)	0.8348(2)	0.6697(8)	0.3297(6)	3.79(8)
C(8)	0.7712(2)	0.6156(10)	0.3417(6)	5.06(11)

TABLE 2—INTERATOMIC DISTANCES (Å) AND INTERBOND ANGLES (°)

C(1)—S	1.686(4)	S—C(1)—N(2)	118.4(3)
C(1)—N(2)	1.343(5)	S—C(1)—N(3)	124.8(3)
C(1)—N(3)	1.321(6)	N(2)—C(1)—N(3)	116.8(4)
N(1)—N(2)	1.389(4)	C(1)—N(2)—N(1)	119.1(3)
N(1)—C(2)	1.280(6)	N(2)—N(1)—C(2)	112.8(4)
C(2)—C(3)	1.460(6)	C(2)—C(3)—C(4)	117.0(4)
C(3)—C(4)	1.427(7)	C(2)—C(3)—C(8)	124.1(4)
C(3)—C(8)	1.390(7)	C(4)—C(3)—C(8)	118.4(4)
C(4)—C(5)	1.394(7)	C(3)—C(4)—C(5)	119.5(4)
C(5)—C(6)	1.417(8)	C(4)—C(5)—C(6)	120.0(5)
C(6)—C(7)	1.397(8)	C(5)—C(6)—C(7)	119.9(5)
C(7)—C(8)	1.380(6)	C(6)—C(7)—C(8)	119.2(4)
		C(7)—C(8)—C(7)	122.5(5)

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