Crystal Structure of (Z)-1-[4-(Trifluoromethyl)benzylidene]thiosemicarbazide

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The compound of (Z)-1-[4-(trifluoromethyl)benzylidene]thiosemicarbazide crystallizes in the triclinic space group $P\bar{1}$ and $Z = 2$ with cell parameters $a = 7.0109(8)\text{\AA}$, $b = 11.7862(13)\text{\AA}$, $c = 14.9095(16)\text{\AA}$, $\alpha = 111.814(2)^\circ$, $\beta = 91.720(2)^\circ$, $\gamma = 101.036(2)^\circ$ and $V = 1115.7(2)\text{\AA}^3$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0438$ and $wR2 = 0.1078$. In the crystal, each molecule is linked by intermolecular N-H...S hydrogen bonds.

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Thiosemicarbazide derivatives are known to be potentially used as antibacterial agents,^{1,2} analytical reagents for the analysis of metals,³ optical storage⁴ and absorbents.⁵ These applications may be explained by the fact that the thiosemicarbazone usually acts as chelating ligands, by which bonding can take place through the sulfur atom and hydrazine nitrogen. Previously, the crystal structure of the isomer (Z)-1-[2-(trifluoromethyl)benzylidene]thiosemicarbazide had already been published.⁶ However, the present crystal structure of (Z)-1-[4-(trifluoromethyl)benzylidene]thiosemicarbazide (**1**) was yet reported. Thus, our present report is to contribute deeper understanding about the crystal structure of (**1**). In addition, the effect of the trifluoromethyl group at the *para* position towards phenyl group is also discussed. Compound **1** (Fig. 1) was synthesized by the reaction between thiosemicarbazide with 2-(trifluoromethyl)benzaldehyde in ethanol, as reported in previous literature.⁷

Being colorless and having a plate-shape single crystal of **1** is suitable for X-ray diffraction analysis, which was obtained from slow evaporation in methanol at room temperature. Data collection and the refinement parameters are listed in Table 1. The hydrogen atoms that bounded to the nitrogen atoms were found from difference Fourier maps and refined freely [refined N-H distance, $0.78(2) - 0.85(2)\text{\AA}$]. The remaining H atoms were positioned geometrically [C-H = $0.93\text{\AA}$] and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All fluorine atoms are disordered over two orientations, with a final refined occupancy

ratio of $0.676(15):0.324(15)$. The disordered atoms were subjected to a similarity restraint (SAME), except for atoms F1X, F2X and F3X. Additionally, the similar-ADP restraint (SIMU) and rigid-bond restraint (DELU) was applied to the F1B, F2B, F3B, F1X, F2X and F3X atoms in the molecule.

In with respect to the title compound, **1** is structurally similar to (Z)-1-[2-(trifluoromethyl)benzylidene]thiosemicarbazide, except for the presence of a trifluoromethyl group at the *para* position attached to a phenyl group.⁶ An ORTEP drawing of the two molecules in the asymmetric unit is shown in Fig. 2. Molecules **1** show a *cis* conformation between the N1A-N2A and N3A-C9A bonds through the N2A-C9A bond. However,

Fig. 1 Chemical diagram of the title compound (**1**).

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Table 1 Crystal data and experimental data

Chemical formula: $\text{C}_9\text{H}_8\text{F}_3\text{N}_3\text{S}$	
Molecular weight: 247.24	
$T = 296(2)\text{K}$	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 7.0109(8)\text{\AA}$	$\alpha = 111.814(2)^\circ$
$b = 11.7862(13)\text{\AA}$	$\beta = 91.720(2)^\circ$
$c = 14.9095(16)\text{\AA}$	$\gamma = 101.036(2)^\circ$
$V = 1115.7(2)\text{\AA}^3$	$Z = 4$
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{\AA}$)	
$\mu(\text{Mo } K\alpha) = 0.31\text{ mm}^{-1}$	
$F(0\ 0\ 0) = 504$	
Crystal size = $0.39 \times 0.38 \times 0.11\text{ mm}^3$	
No. of reflections collected = 29457	
No. of independent reflections = 5104	
θ range for data collection: 1.48 to 27.53°	
Data/Restraints/Parameters = 5104/15/368	
Goodness-of-fit on $F^2 = 1.008$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0438$, $wR2 = 0.1078$	
R indices (all data): $R1 = 0.0848$, $wR2 = 0.1327$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.289\text{ e}\text{\AA}^{-3}$	
$(\Delta\rho)_{\text{min}} = -0.174\text{ e}\text{\AA}^{-3}$	
Measurement: Bruker SMART CCD	
Programs system: SHELXTL-97, SADABS	
Structure determination: SHELXS-97	
CCDC deposition number: 1507979	

Table 2 Selected geometric parameters, bond length and angles (Å, °)

Bond	Bond length/Å	Bond	Bond angle/°
C8A-N1A	1.272(3)	C5A-C8A-N1A	122.30(2)
N1A-N2A	1.372(2)	C8A-N1A-N2A	115.21(17)
N2A-C9A	1.339(2)	N1A-N2A-C9A	121.06(17)
C9A-N3A	1.311(2)	N2A-C9A-N3A	118.09(18)
C9A-S1A	1.690(18)	N2A-C9A-S1A	123.34(16)
C8B-N1B	1.265(2)	C5B-C8B-N1B	121.60(2)
N1B-N2B	1.373(2)	C8B-N1B-N2B	116.49(17)
N2B-C9B	1.340(2)	N1B-N2B-C9B	120.01(17)
C9B-N3B	1.308(2)	N2B-C9B-N3B	117.28(17)
C9A-S1A	1.685(18)	N2B-C9B-S1B	119.47(14)

Fig. 2 ORTEP structure of two molecules in the asymmetric unit for (Z)-1-[4-(trifluoromethyl)benzylidene]thiosemicarbazide, showing 50% probability ellipsoids.

both the N1A-N2A and C9A-S1A bonds are in a *trans* conformation through the N2A-C9A bond. In addition, another asymmetric unit maintains the conformations. The plane (defined by S1A/N1A/N2A/N3A/C2A/.../C9A) for the first residue is almost planar with a maximum deviation of $-0.034(3)$ Å for atom C2A, as compared with the second residue plane (defined by N1B/C1B/.../C8B) with a maximum deviation of $0.046(5)$ Å for atom C1B, and makes a dihedral angle of $21.51(9)^\circ$. Both thioureido (defined by S1B/N2B/N3B/C9B) and N1B/C1B/.../C8B fragments for the second residue have a maximum deviation of $0.046(5)$ Å for atom C1B, and make dihedral angles of $19.34(11)^\circ$. The double-bond lengths for C8A-N1A and C8B-N1B are $1.272(3)$ and $1.265(2)$ Å, respectively. This is slightly shorter compared with C=N ($1.279(3)$ Å) in the other isomer.⁶ Meanwhile, the bond angles for C8A-N1A-N2A and C8B-N1B-N2B are $115.21(17)$ and $116.49(17)^\circ$, respectively, and have no significant differences with another reported isomer, which has a bond angle of $116.0(2)^\circ$.⁶ Other bond lengths and angles are in the normal ranges.⁸ This study reveals that the position of the trifluoromethyl group at either *ortho* or *para* of phenyl does not have any significant effects towards the bond length and angles of the

Fig. 3 Packing of structure 1, showing molecules connected by N-H...S hydrogen bonds (dashed lines).

Table 3 Hydrogen-bond geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
N2A-H1NA...S1A ⁱ	0.81	2.60	3.3513	155
N3A-H3NA...S1B ⁱⁱ	0.87	2.59	3.4505	173
N3B-H3NB...S1A ⁱⁱⁱ	0.85	2.49	3.3295	171
N2B-H1NB...S1B ^{iv}	0.85	2.59	3.4168	165

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

C=N-N moiety. The introduction of trifluoromethyl at the *para* position of benzyl forbids the formation of intramolecular hydrogen bonds, as similarly observed in the case of (Z)-1-[2-(trifluoromethyl)benzylidene]thiosemicarbazide.⁶ In the crystal structure of 1, each of molecule is linked by four intermolecular hydrogen bonds, namely N2A-H1NA...S1A, N3A-H3NA...S1B, N3B-H3NB...S1A and N2B-H1NB...S1B (symmetry codes as in Table 3) to form a one-dimensional wave-like chain parallel to (032) plane (Fig. 2).

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