Crystal Structure of 4-Hydroxy-3-methoxybenzaldehyde-4-methylthiosemicarbazone

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The structure of 4-hydroxy-3-methoxybenzaldehyde-4-methylthiosemicarbazone (VAMTSC) was determined by X-ray crystallography. The molecular structure matches the asymmetric unit, and the compound crystallizes in a monoclinic system. It was characterized thus: $P2_1/c$, $a = 8.4960(3)$, $b = 8.5040(2)$, $c = 17.2236(6)$ Å, $\beta = 111.513(2)^\circ$, $Z = 4$, $V = 1157.71(6)$ Å³. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0403$ and $wR2 = 0.078$.

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Thiosemicarbazone derivatives can adopt various coordination modes as N,S -donors, and are an important subject research concerning pharmacological studies.^{1,2} As a part of our study and on-going project on the synthesis of thiosemicarbazone derivatives, we report herein the crystal structure of 4-methylthiosemicarbazone derivative from vanillin (4-hydroxy-3-methoxybenzaldehyde), a primary component of the extract of the vanilla bean. The title compound synthesis was adapted from a procedure reported previously.³ The title compound was prepared by the hydrochloric acid-catalyzed reaction of a mixture of vanillin (8.83 mmol) and 4-methylthiosemicarbazide (8.83 mmol) in ethanol (50 mL) being refluxed for 6 h. After cooling and filtering, crystals of the VAMTSC (Fig. 1) suitable for X-ray diffraction were obtained by slow evaporation of the solvent.

The intensities for the X-ray determinations were collected on a Kappa CCD diffractometer. The structure was solved using SHELXS. The absorption correction was performed by a multi-scan method ($T_{\min}/T_{\max} = 0.916/0.988$). Crystal data and details concerning data collection are given in Table 1. All H atoms were located in a difference map but were positioned with the idealized geometry (methyl and O-H H atoms allowed to rotate)

Fig. 1 Chemical diagram of the title compound.

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and were refined isotropic with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (for aromatic C atoms and N atoms) and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ (for methyl C atoms and for the hydroxyl H atom) using a riding model with C-H =

Table 1 Crystal and experimental data

Chemical formula = $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$
Formula weight = 239.29
$T = 123(2)\text{K}$
Crystal system: monoclinic
Space group: $P2_1/c$
$a = 8.4960(3)\text{\AA}$
$b = 8.5040(2)\text{\AA}$
$c = 17.2236(6)\text{\AA}$
$\beta = 111.513(2)^\circ$
$Z = 4$
$V = 1157.71(6)\text{\AA}^3$
$D_x = 1.373\text{ g/cm}^3$
Radiation = Mo K_α ($\lambda = 0.71073\text{ \AA}$)
$\mu_{\text{Mo } K_\alpha} = 0.269\text{ mm}^{-1}$
$F(0\ 0\ 0) = 504$
Crystal size = $0.28 \times 0.14 \times 0.11\text{ mm}^3$
No. of reflections collected = 12991
No. of independent reflections = 2626
θ range for data collections = 3.41 to 27.47°
Data/Restraints/Parameters = 2626/0/148
Goodness-of-fit on $F^2 = 1.103$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0403$, $wR2 = 0.0780$
R indices (all data): $R1 = 0.0682$, $wR2 = 0.0876$
$(\Delta/\sigma)_{\max} = 0.001$
$(\Delta\rho)_{\max} = 0.24\text{ e}^{-\text{\AA}^{-3}}$
$(\Delta\rho)_{\min} = -0.28\text{ e}^{-\text{\AA}^{-3}}$
Measurement = Kappa CCD diffractometer
Program system = COLLECT (NONIUS, 1998), HKL, DENZO and SCALEPACK (Otwinowski and Minor, 1997)
Structure determination = SHELXS (Sheldrick, 2008)
Refinement = SHELXL (Sheldrick, 2008)
Absorption correction = multi-scan (Blessing, 1997)
CCDC deposition number = 1019958

Fig. 2 ORTEP structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level.

Table 2 Hydrogen-bond geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
O2—HO2...S1 ⁱ	0.84	2.38	3.2066(14)	168.1
N2—HN2...S1 ⁱⁱ	0.88	2.56	3.3963(15)	159.3
N3—HN3...O1 ⁱⁱⁱ	0.88	2.42	3.0155(18)	125.2

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

0.95 Å for aromatic, C-H = 0.98 Å for methyl, N-H = 0.88 Å for amine and hydrazine, and O-H = 0.84 Å for the hydroxyl H atoms.

In Fig. 2 an ORTEP drawing of the title compound, $C_{10}H_{13}N_3O_2S$, is given. The C-S-N(H)-N linkage is nearly planar with the torsion angle being $176.37(12)^\circ$. The selected bond angles of $C1-C7-N1 = 121.42(16)^\circ$, $C7-N1-N2 = 116.17(14)^\circ$ and $N2-C8-N3 = 117.15(15)^\circ$ suggest a sp^2 hybridization for the C7, N1 and C8 atoms. The selected bond distances $C7-N1 = 1.280(2)\text{Å}$ and $C8-S1 = 1.7019(17)\text{Å}$ are consistent with a double-bond character, while $N1-N2 = 1.3809(19)\text{Å}$ and $N2-C8 = 1.348(2)\text{Å}$ are consistent with a single-bond character.^{2,4} They support the hybridization and geometry attributed to the atoms of the thiosemicarbazone group.

The molecule deviates slightly from the ideal planarity with the maximum distance from the mean plane through the non-H atoms being to $0.2109(14)\text{Å}$ for O2. The maximum deviation from the mean plane of the non-H atoms for the thiosemicarbazone fragment amount to $0.0598(14)\text{Å}$ for N3 and the dihedral angle between this plane and the aromatic ring is

Fig. 3 Packing diagram of the title compound showing a centrosymmetric herringbone pattern viewed along the c -axis.

$9.28(10)^\circ$. The molecular units are linked by pairs of N-H...S hydrogen bonds, and related by centers of symmetry building dimers. Additionally, the dimers are linked by N-H...O and O-H...S hydrogen bonds, and the crystal structure of the title compound becomes to a two-dimensional hydrogen-bonded network with a $[1\ 0\ 1]$ orientation. One intramolecular H-bond is also observed, with the HN3...N1 distance amounting to $2.244(2)\text{Å}$, a *trans* configuration for the N1-N2 bond is also observed. The hydrogen-bonding data are summarized in Table 2.

Finally, when viewed along the c -axis the crystal packing shows a centrosymmetric herringbone pattern along the a -axis (Fig. 3), which is well reported in the literature.^{2,4}

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