

КРАТКИЕ СООБЩЕНИЯ

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STRUCTURAL ANALYSIS OF ETHYL
2-Z-PHENYLHYDRAZONO-3-E-METHYLTHIO(THIOXO)METHYLHYDRAZONE-BUTANOATE

P. Wu

Department of Chemistry, Dezhou College, Shandong; Key Laboratory of Coordination Chemistry and Functional Materials at Universities of Shandong, P. R. China
E-mail: pingwu.dzu@gmail.com

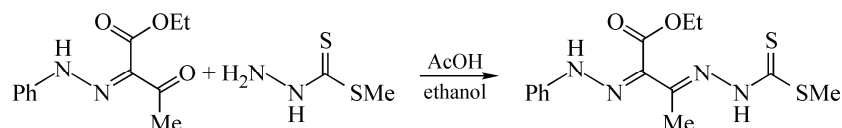
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A new compound of ethyl 2-Z-phenylhydrazono-3-E-methylthio(thioxo) methylhydrazono-butanoate is synthesized *via* the reaction between ethyl 2-Z-phenylhydrazono-3-oxo-butanoate and *S*-methylthiocarbamate at room temperature. A single crystal of the titled compound is obtained and the structure is determined by X-ray diffraction. It belongs to a monoclinic $P2_1$ space group with the cell parameters: $a = 5.335(1) \text{ \AA}$, $b = 15.907(4) \text{ \AA}$, $c = 9.507(2) \text{ \AA}$, $\beta = 90.21(1)^\circ$, $V = 806.8(4) \text{ \AA}^3$. A one-dimensional parallel structure is constructed by an unclassic hydrogen bond and a weak $p-\pi$ interaction.

Keywords: X-ray diffraction, phenylhydrazono, methylhydrazono, butanoate.

Alkyl 2-phenylhydrazono-3-oxo-butanoates can be easily synthesized by the reaction of aromatic amines and alkyl acetoacetates with the aid of nitrous acid [1—5]. These compounds can further reflux with substituted hydrazines to give the corresponding pyrazoles, which have attracted much attention for therapeutic activities, such as antitumor, antiviral, analgesic, and anti-inflammatory properties [6—9]. Besides, with the *N*- and *O*-electron-donating atoms, pyrazoles can also be applied in coordination chemistry. However, if carried out at room temperature, linear compounds, rather than pyrazoles, will be obtained due to the reaction between substituted hydrazines and alkyl 2-phenylhydrazono-3-oxo-butanoates. As a part of our continuous research work [10], herein, a new compound of ethyl 2-Z-phenylhydrazono-3-E-methylthio(thioxo)methylhydrazono-butanoate is synthesized by the reaction of ethyl 2-Z-phenylhydrazono-3-oxo-butanoate and *S*-methylthiocarbamate at room temperature. Its structure is revealed by X-ray crystallography.

Experimental. The reactant of ethyl 2-Z-phenylhydrazono-3-oxo-butanoate was synthesized as reported [1—5]. The procedure to synthesize the titled compound is shown below, in Scheme 1.



Scheme 1. Synthesis of the titled compound

To a mixed solution of ethyl 2-Z-phenylhydrazono-3-oxo-butanoate (2.0 mmol) and *S*-methylthiocarbamate (2.0 mmol) dissolved in 10 ml of ethanol a few drops of acetic acid is added. This solution is stirred at r.t. for 24 h. The solvent is removed to obtain the crude product which is purified by flash column to give the pure product with a yield of 70 %. The pure product is redissolved in di-

chloromethane, which is slowly evaporated at r.t. to give the desired crystal with light yellow color. IR (KBr): 3150, 3002, 1715, 1652, 1505, 1270, 1114, 1023, 960 cm^{-1} ; Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$: C, 49.68; H, 5.36; N, 16.55. Found: C, 49.75; H, 5.33; N, 16.45.

Table 1

Crystal data and structure refinement for the titled compound

Chemical formula	$\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$
Molecular weight	338.44
Crystal system	Monoclinic
Space group	$P2_1$
$a, b, c, \text{\AA}$	5.335(1), 15.907(4), 9.507(2)
β , deg.	90.21(1)
T , K	296(2)
$V, \text{\AA}^3$	806.8(4)
Z	2
$D_c, \text{g}\cdot\text{cm}^{-3}$	1.389
μ, mm^{-1}	0.342
$F(000)$	356
θ range, deg.	2.5–27.1
Index ranges (h, k, l)	–6/6, –19/19, –11/11
R_{int}	0.0821
Refined data, parameter, restriction	3142, 202, 3
Observed reflections with $I > 2\sigma(I)$	2897
GOOF	1.150
Final R factor [$I > 2\sigma(I)$]	$R_1 = 0.0919, wR_2 = 0.2629$
R factor (all data)	$R_1 = 0.0982, wR_2 = 0.2671$
$(\Delta\rho)_{\text{max}} / (\Delta\rho)_{\text{min}}, \text{e}/\text{\AA}^3$	0.627 / –0.580

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

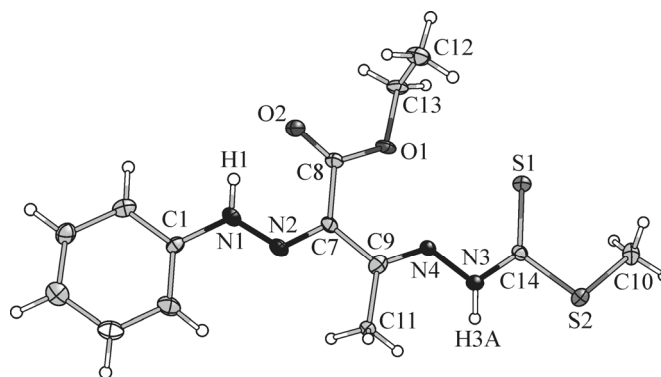
$$^b wR_2 = \frac{|\sum w(|F_o|^2 - |F_c|^2)|}{\sum w(F_o)^2}^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]. \text{ } P = (F_o^2 + 2F_c^2)/3.$$

Table 2

Selected geometric parameters (\AA , deg.)

C1—N1	1.416(4)	C7—N2	1.294(4)	C7—C9	1.486(4)
C7—C8	1.501(4)	C8—O2	1.199(4)	C8—O1	1.333(4)
C9—N4	1.268(4)	C9—C11	1.513(5)	C10—S2	1.810(4)
C14—N3	1.333(4)	C14—S1	1.696(3)	C14—S2	1.776(3)
N1—N2	1.312(3)	N3—N4	1.376(4)	C13—O1	1.476(4)
N2—C7—C9	114.4(3)	N2—C7—C8	122.1(3)	C9—C7—C8	123.6(3)
O2—C8—O1	124.1(3)	O2—C8—C7	122.5(3)	O1—C8—C7	113.4(3)
N4—C9—C7	121.9(3)	N4—C9—C11	119.7(3)	C7—C9—C11	118.3(3)
N3—C14—S1	128.0(3)	N3—C14—S2	109.2(2)	S1—C14—S2	122.7(2)
N2—N1—C1	120.7(3)	C14—S2—C10	103.9(1)	C9—N4—N3	125.2(3)
N1—N2—C7	121.3(3)	C14—N3—N4	111.7(3)	C8—O1—C13	118.0(3)

Fig. 1. Molecular structure of the titled compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level



IR and elemental analysis. FT-IR spectra were recorded in the range 400—4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer.

X-ray Crystallography. A Bruker Smart Apex II CCD area-detector diffractometer is used for the crystallographic data collections with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K using the ω -scan technique. The diffraction data were integrated using the SAINT program [11], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [12]. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [13]. Hydrogen atoms were generated geometrically. Table 1 gives the crystal data and structural refinement for the titled compound, while Table 2 collects the selected bond lengths and bond angles.

Results and discussion. The structure of the titled compound is depicted in Fig. 1 in a monoclinic crystal system and the space group $P2_1$.

This molecule is revealed to be nearly planar (disregarding hydrogen atoms), except for C12, which is $81.4(4)^\circ$ deviated from the plane. The planarity of this molecule can be confirmed by torsion angles C9—C7—C8—O1 of $8.7(4)^\circ$, C1—N1—N2—C7 of $179.3(3)^\circ$, N2—C7—C9—N4 of $-179.9(3)^\circ$, C9—N4—N3—C14 of $178.4(3)^\circ$, N4—N3—C14—S2 of $174.1(2)^\circ$, N3—C14—S2—C10 of $174.2(2)^\circ$, and C11—C9—C7—C8 of $176.4(3)^\circ$.

The C7—N2 and C9—N4 bond lengths are $1.294(4) \text{ \AA}$ and $1.268(4) \text{ \AA}$ respectively, which conform to the typical values of C=N double bonds. Meanwhile, the N1—N2 and N3—N4 bonds are $1.312(3) \text{ \AA}$ and $1.376(4) \text{ \AA}$, indicating two single bonds. Moreover, the C14—S1 and C14—S2 bond distances are $1.696(3) \text{ \AA}$ and $1.776(3) \text{ \AA}$, which means that C14=S1 is a double bond and C14—S2 is a single bond.

Two intramolecular hydrogen bonds, namely N1—H1 \cdots O2 and C11—H11A \cdots N3, were found to stabilize the crystal structure (Table 3). The N1 \cdots O2 and C11 \cdots N3 interatomic distances are found to be $2.577(4) \text{ \AA}$ and $2.818(5) \text{ \AA}$ respectively. The acceptor distances are $1.908(2) \text{ \AA}$ and $2.440(3) \text{ \AA}$ for H1 \cdots O2 and H11A \cdots N3. The bond angles for each hydrogen bond are $133.6(2)^\circ$ and $103.2(2)^\circ$.

Apart from intramolecular hydrogen bonds, two intermolecular weak interactions are also revealed, being an unclassic hydrogen bond of C10—H10A \cdots N3' and a possible p — π interaction between S1 and the C7'—C8' bond. For C10—H10A \cdots N3', the interatomic distances are $3.495(5) \text{ \AA}$ and $2.733(3) \text{ \AA}$ for C10 \cdots N3' and H10A \cdots N3' respectively. This weak interaction, together with the possible p — π interactions, will construct a one-dimensional parallel structure, as shown in Fig. 2.

Table 3

Hydrogen bonding geometry in the titled compound (\AA , deg.)

Entry	D—H \cdots A	D \cdots H	H \cdots A	D \cdots A	D—H \cdots A	Symmetry Codes
1	N1—H1 \cdots O2	0.86	1.908(2)	2.577(4)	133.6(2)	
2	C11—H11A \cdots N3	0.96	2.440(3)	2.818(5)	103.2(2)	
3	C10—H10A \cdots N3'	0.96	2.733(3)	3.495(5)	136.7(2)	$-x, 1/2+y, -z$

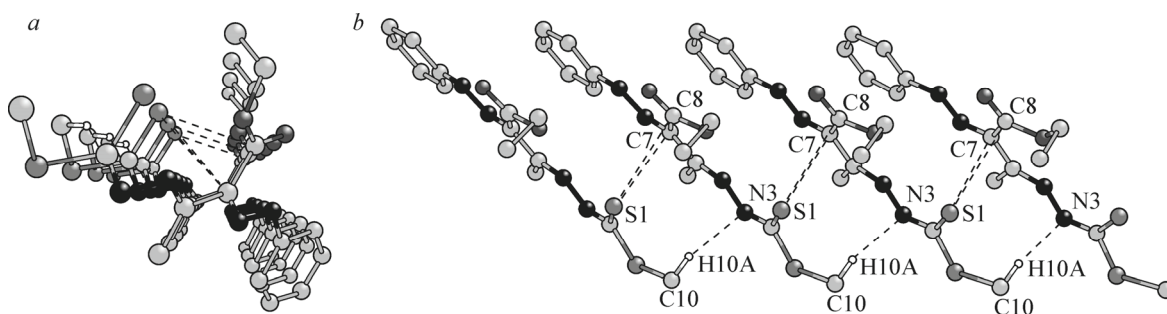


Fig. 2. One-dimensional parallel structure of the titled compound: viewed along the *a* axis (a), viewed along the *b* axis (b)

Supplementary material. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 888553, and is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif

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