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Acetone 4-Benzylthiosemicarbazone의 결정 및 분자구조

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The Crystal and Molecular Structure of Acetone 4-Benzylthiosemicarbazone

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요 약. Acetone 4-benzylthiosemicarbazone의 결정 구조를 단결정 X-선 회절법에 의하여 연구하였다. 결정은 단사축계에 속하며, 공간군은 $P2_1/c$, 단위세포내에는 4개의 분자가 들어있고 단위세포 상수는 $a=10.249(7)$, $b=11.403(9)$, $c=10.149(7)$ Å, $\beta=90.1(1)^{\circ}$이다. 회절농도는 4축자동회절장치에 의하여 얻었다. 분자구조는 직접법에 의하여 밝혔으며, 최소자승법으로 정밀화한 결과 1554반점에 대하여 최종 신뢰도 R값은 0.045 이었다. 분자내에서 S-C(8)-N(2)-N(3)-C(9)-C(10) 원자들은 zigzag planar chain 을 이루고 있다. 분자들은 2종류의 수소결합에 의하여 연결되어 있다. 하나는 N-H...S 분자간 수소결합으로 길이는 3.555Å이며 분자들을 이량체 처럼 붙들어주고 있다. 다른 하나는 N-H...N 분자내수소결합으로 길이는 2.568Å 이다. 이화합물의 분자구조를 구조가 이미 밝혀진 다른 thiosemicarbazone 유도체들과 비교 고찰하였다.

ABSTRACT. The crystal and molecular structure of acetone 4-benzylthiosemicarbazone, $C_{11}H_{15}N_3S$, has been determined by the single crystal X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions, $a=10.249(7)$, $b=11.403(9)$, $c=10.149(7)$ Å, $\beta=90.9(1)^{\circ}$ and $z=4$. The intensities were collected on an automatic four-circle diffractometer with graphite-monochromated Mo-K_{α} radiation. The structure was solved by direct methods and refined by full matrix least-squares methods. The final R was 0.045 for 1554 observed reflections. S-C(8)-N(2)-N(3)-C(9)-C(10) atoms make a zigzag planar chain. There are no unusual bond lengths and angles. There are two independent hydrogen bonds in the crystal structure. One is N-H...S intermolecular hydrogen bond with the length of 3.555Å and makes dimer-like units. The other is N-H...N intramolecular hydrogen bond with the length of 2.568Å. The structure was compared with those of other thiosemicarbazone derivatives.

INTRODUCTION

This work is part of a program concerned with the crystal and molecular structures of the thiosemicarbazone derivatives*. Much information of chemical interest is hidden in crystal structures because they represent minimum energy arrangements, and whereas little can be inferred from a single structure, certain trends become apparent if enough structures are available. The crystal structures of fourteen alkyl and arylthiosemicarbazones[1~12] have been determined by the X-ray diffraction methods so far.

Palenik *et al*[1] reported general features of thiosemicarbazone groups, but they discussed only five structures. Therefore, a comparison of the results of fourteen crystal structure determinations, including that for acetone 4-benzylthiosemicarbazone which is presently reported, may suggest some generalization with regard to the electronic structures, conformational properties and hopefully biological activities of the thiosemicarbazones. We have already discussed the hydrogen bondings of the thiosemicarbazones in the crystalline state[3].

EXPERIMENTAL

A sample of acetone 4-benzylthiosemicarbazone (ABTC) was kindly supplied by Professor Y. S. Chough of Seoul National University and recrystallized as pale yellow prisms from an acetone solution. Oscillation and Weissenberg photographs showed the crystal system to be monoclinic. The space group $P2_1/c$ was indicated by the absence of reflections *h0l* with *l* odd and *0k0* with *k* odd. The density was measured by the floatation method in a mixture of carbon tetrachloride and benzene.

A crystal with approximate dimensions of 0.5×0.5×0.4mm was selected for the data collections. The intensity data were collected on a Rigaku AFC Diffractometer with graphite monochromated Mo-K_α radiation in the range of $2\theta \leq 50°$. Reflections were scanned at a rate of 8°/min. in 2θ and over a scan width of $(1.2+0.5\tan\theta)°$ in ω in the ω-2θ scan mode. Three standard reflections were measured every 50 reflections and were used to monitor the crystal alignment and stability.

The lattice constants were refined by the least-squares method from the 2θ values for 20 reflections. The intensity data were reduced to structure factors by the application of Lorentz-polarization factors[13]. 1554 reflections had $|F_0| > 3\sigma|F_0|$ and were used in the structure determination and refinements. The crystal data are given in *Table* 1.

The structure was solved by the direct method program MULTAN[14] using 182 reflections whose E values were greater than 1.45. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of all the non-hydrogen atoms. Six cycles of isotropic refine-

Table 1. Crystal data

Acetone 4-benzylthiosemicarbazone; $C_{11}H_{15}N_3S$
MW; 221.28
Unit-cell parameters; a=10.249(7)Å, b=11.403(9), c=10.149(7), β=90.9(1)°, Z=4
μ=2.04cm^{-1}
Crystal system; monoclinic
Space group; $P2_1/c$ from systematic absences *hol* if $l=2n+1$, *oko* if $k=2n+1$
Density; Dc=1.239 gcm^{-3}, Dm=1.25gcm^{-3}.

*Nomenclature of the thiosemicarbazone derivatives is referred to "Nomenclature of Organic Chemistry", part 1, pp. 329-332, Korean Chemical Society, 1981. This title compound, R_1-NH-CS-NH-N=CR_2R_3 (positions 4, 3, 2, 1), where $R_1=C_6H_5CH_2$ and $R_2=R_3=CH_3$, can be named using the name of the thiosemicarbazone or thiosemicarbazide derivatives such as (1) acetone 4-benzylthiosemicarbazone or (2) 1-isopropylidene-4-benzylthiosemicarbazide.

ments reduced R value to 0.149. A difference map after two more cycles of anisotropic refinements revealed all the hydrogen positions. The final full matrix least-squares refinements in which the non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically reduced the R value to 0.045. All refinements were carried out with the program SHELX 76[15].

The fractional atomic coordinates and the thermal parameters with their estimated standard deviations are listed in *Table* 2.

Table 2*a*. Atomic coordinates for the non-hydrogen atoms of acetone 4-benzylthiosemicarbazone. The e. s. d's are given in parentheses.

Atoms	X	Y	Z
S	0.5994(1)	0.9757(1)	0.6831(1)
N(1)	0.5841(2)	0.7456(2)	0.7321(2)
N(2)	0.4464(2)	0.8161(2)	0.5742(2)
N(3)	0.4180(2)	0.6992(2)	0.5471(2)
C(1)	1.0215(4)	0.5542(5)	0.7141(6)
C(2)	0.9548(4)	0.5217(4)	0.8223(5)
C(3)	0.8476(3)	0.5830(4)	0.8619(3)
C(4)	0.8046)2)	0.6795(2)	0.7911(3)
C(5)	0.8725(3)	0.7118(3)	0.6807(3)
C(6)	0.9795(4)	0.6492(5)	0.6426(5)
C(7)	0.6861(3)	0.7463(3)	0.8324(3)
C(8)	0.5417(2)	0.8382(2)	0.6634(2)
C(9)	0.3294(2)	0.6746(2)	0.4628(2)
C(10)	0.3089(4)	0.5470(3)	0.4366(4)
C(11)	0.2487(4)	0.7601(3)	0.3876(4)

Table 2*b*. Atomic coordinates and isotropic thermal parameters U(×10³Å²) for the hydrogen atoms.

Atoms	X	Y	Z	U
H(C(1))	1.085(4)	0.519(5)	0.688(5)	172(24)
H(C(2))	0.976(3)	0.453(3)	0.880(4)	107(13)
H(C(3))	0.796(2)	0.559(2)	0.938(3)	71 (9)
H(C(5))	0.838(2)	0.771(3)	0.635(3)	66(10)
H(C(6))	0.021(3)	0.671(2)	0.566(3)	85(11)
H(C(7))	0.648(3)	0.715(2)	0.910(3)	76(10)
H'(C(7))	0.707(2)	0.826(2)	0.853(2)	61 (8)
H(N(1))	0.546(2)	0.682(2)	0.707(2)	63 (9)
H(N(2))	0.425(2)	0.864(2)	0.527(2)	39 (7)
H(C(10))	0.363(2)	0.499(2)	0.493(3)	62 (9)
H'(C(10))	0.218(3)	0.531(3)	0.444(3)	92(12)
H"(C(10))	0.318(3)	0.532(3)	0.356(4)	87(14)
H(C(11)	0.221(4)	0.827(4)	0.441(4)	126(16)
H'(C(11))	0.169(3)	0.727(3)	0.361(3)	91(11)
H"(C(11))	0.279(3)	0.799(3)	0.323(4)	105(14)

Table 2*c*. Anistropic thermal parameters for non-hydrogen atoms.
$U(X10^4Å^2)=\exp-2\pi^2(U_{11}h^2\ a^{*2}+U_{22}k^2\ b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2UCl_{13}hla^*c^*+2U_{12}hka^*b^*)$

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	684(4)	313(3)	584(4)	24(3)	−115(3)	−82(3)
N(1)	478(12)	328(11)	480(13)	23(10)	93(10)	14(11)
N(2)	502(13)	267(11)	520(14)	48(11)	−87(11)	−7(10)
N(3)	525(12)	274(10)	506(13)	9(9)	−68(10)	−47(9)
C(1)	539(25)	1264(43)	1080(39)	−501(35)	−172(25)	266(26)
C(2)	998(30)	809(27)	824(28)	−178(24)	−404(25)	442(24)
C(3)	783(21)	506(18)	452(17)	−40(14)	−150(16)	120(17)
C(4)	442(14)	343(13)	429(15)	−63(12)	−113(12)	−56(11)
C(5)	522(18)	549(19)	271(22)	44(17)	93(17)	−116(15)
C(6)	606(24)	1084(35)	917(32)	−164(27)	205(24)	−212(24)
C(7)	577(17)	494(17)	429(17)	−29(15)	−45(14)	57(16)
C(8)	404(13)	332(13)	367(14)	−12(11)	37(11)	−1(10)
C(9)	438(13)	357(13)	448(14)	15(11)	−36(11)	−66(11)
C(10)	700(23)	436(17)	702(24)	−33(16)	−123(19)	−141(15)
C(11)	577(19)	544(19)	824(25)	120(19)	233(19)	122(17)

RESULTS AND DISCUSSION

The molecular conformation and atomic numbering are shown in *Fig.* 1.[16] The bond lengths and angles (*Fig* 2.) are similar to those found in the related compounds.

The bond lengths and angles found in the thiosemicarbazide chain of various thiosemicarbazones[1~12] have been tabulated in *Table* 3. The average C(8)-S bond length of 1.687(10) Å shows the partial double bond character of the C-S bond. Excluding acetone 4-benzylthio-

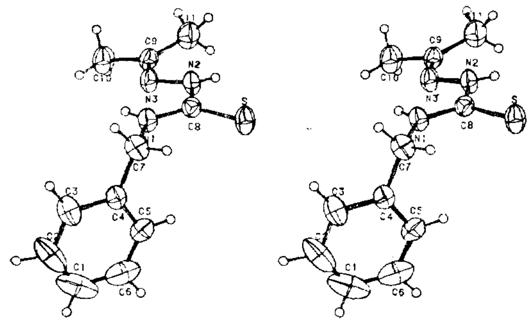


Fig. 1. Molecular conformation and atomic numbering in acetone 4-benzylthiosemicarbazone.

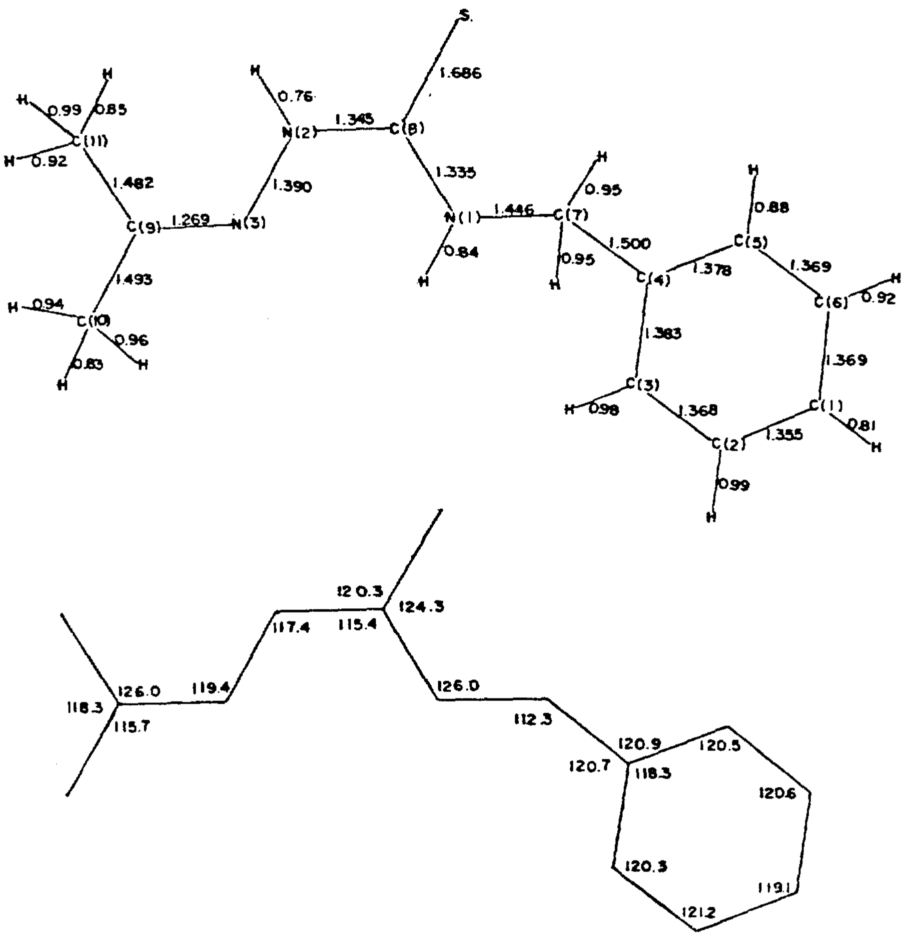
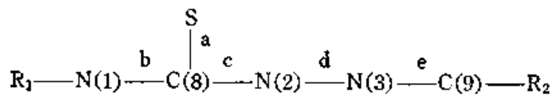


Fig. 2. Bond lengths(Å) and bond angles (°) in acetone 4-benzylthiosemicarbazone. Average e. s. d's are 0.003Å and 0.2° for acetone thiosemicarbazone part, and 0.005Å 0.4 for benzyl part.

Table 3. Bond lengths (Å) and angles (°) observed in various thiosemicarbazones.



Compound	a	b	c	d	c	∠ab	∠ac	∠bc	∠cd	∠de
I	1.689	1.335	1.345	1.390	1.269	124.3	120.3	115.4	117.4	119.4
II	1.690	1.334	1.342	1.398	1.286	122.8	119.3	117.8	117.6	116.6
III(A)+	1.687	1.305	1.359	1.371	1.294	124.3	118.1	117.6	119.1	117.3
	1.692	1.310	1.351	1.371	1.285	123.4	118.2	118.3	119.4	115.8
(B)	1.682	1.311	1.352	1.365	1.290	124.3	117.8	117.9	119.9	117.4
	1.689	1.314	1.351	1.379	1.284	124.1	118.1	117.8	119.4	115.6
IV	1.700	1.322	1.346	1.384	1.278	124.1	118.6	117.3	120.9	114.6
V	1.697	1.316	1.361	1.381	1.284	124.6	116.9	118.5	119.4	113.5
VI	1.706	1.307	1.336	1.379	1.270	122.5	118.2	119.2	118.7	115.1
VII	1.678	1.329	1.354	1.365	1.275	123.6	119.8	116.6	118.8	116.8
VIII	1.687	1.318	1.349	1.369	1.318	123.7	118.7	117.6	120.6	115.3
IX	1.679	1.345	1.338	1.372	1.261	123.7	120.3	116.1	121.2	115.7
X	1.675	1.345	1.340	1.372	1.276	123.7	119.4	116.9	120.2	115.3
XI	1.67	1.28	1.38	1.36	1.28	126.4	117.4	116.2	118.3	117.6
XII*	1.75	1.24	1.40	1.35	1.28	124	118	118	119	116
XIII*	1.66	1.35	1.35	1.41	1.26	124.1	121.8	114.1	118.5	114.9
XIV(A)*	1.71	1.40	1.37	1.46	1.32	124.5	119.4	116.0	120.6	114.3
(B)	1.74	1.39	1.41	1.44	1.27	126.6	118.4	115.1	117.7	116.5
mean	1.687	1.319	1.350	1.375	1.282	124.0	118.7	117.4	119.4	116.1
(e.s.d.)	(10)	(17)	(11)	(10)	(14)	(9)	(10)	(10)	(12)	(15)

I: acetone 4-benzylthiosemicarbazone. II: acetone thiosemicarbazone[1]. III: 2-keto-3-ethoxybutyraldehyde bis (thiosemicarbazone)[2]. IV: *p*-aminobenzaldehyde 4-cyclohexylthiosemicarbazone[3]. V: *p*-acetylaminobenzaldehyde thiosemicarbazone[4]. VI: 5-hydroxy-2-formylpyridine thiosemicarbazone sesquihydrate[1]. VII: 4-formylpyridine thiosemicarbazone[5]. VIII: 2-formyl-4-morpholinopyridine thiosemicarbazone[6]. IX: 2-formyl-5-benzylpyridine thiosemicarbazone[7]. X: 2-formyl-4-phenylpyridine thiosemicarbazone dimethyl formamide[8]. XI: 1-formyl-5-amino-4-methylisoquinoline thiosemicarbazone hydrochloride[9]. XII: 0-chlorobenzaldehyde 4-cyclohexylthiosemicarbazone[10] XIII: salicylaldehyde 4-piperidinothiosemicarbazone[11]. XIV: *p*-dimethylaminobenzaldehyde 4-p-ethoxyphenylthiosemicarbazone[12].

+A and B two molecules in the asymmetric unit.

*structures done by photographic methods. Due to the large standard deviations, the observed values were excluded from the calculations of average values.

semicarbazone and acetone thiosemicarbazone (ATC)[1]. the average N(2)-N(3) bond length is 1.372(7)Å, which is significantly shorter than the values of 1.390 and 1.398Å for ABTC and ATC, respectively. The most obvious explanation for the shortened N(2)-N(3) bond would involve an interaction with the group on C(9). Therefore, our study of thiosemicarbazones suggests that certain thiosemicarbazones (usually those containing aryl groups on C(9)) can be treated as extensively delocalized systems. The average N(3)-C(9) bond length of 1.282(14)Å is close to a C-N double bond length.

In most thiosemicarbazones, the C(8)-N bonds in the chain are significantly different. The averages are: C(8)-N(1) is 1.319(17) and C(8)-N(2) is 1.350(11)Å. This difference is reasonable since in the case of N(1), we have

Table 4. Conformational angles in degrees in acetone 4-benzylthiosemicarbazone.

C(5)-C(4)-C(7)-N(1)	60.0°
C(4)-C(7)-N(1)-C(8)	112.9
C(7)-N(1)-C(8)-S	0.8
C(7)-N(1)-C(8)-N(2)	179.4
S-C(8)-N(2)-N(3)	169.7
N(1)-C(8)-N(2)-N(3)	10.6
C(8)-N(2)-N(3)-C(9)	179.5
N(2)-N(3)-C(9)-C(10)	177.9
N(2)-N(3)-C(9)-C(11)	0.5

Table 5. Equations of the least squares planes with atomic displacements in acetone 4-benzylthiosemicarbazone. The plane constants referred to orthogonal axes are in Å.

(1) Benzene group
$0.577x+0.593y+0.562z=13.788$
C(1) 0.004Å C(2) −0.003 C(3) 0.000
C(4) 0.001 C(5) 0.001 C(6) −0.003
C(7)* −0.017

(2) Formylthiosemicarbazone group
$0.734x-0.146y-0.663z=-1.842$
S 0.050 C(8) −0.020 C(9) 0.028
N(1) −0.017 N(2) −0.090 N(3) 0.077
C(7)* 0.063

(3) Acetone group
$-0.693x-0.026y+0.720z=0.884$
N(3) −0.003 C(9) 0.008 C(10) −0.002
C(11) −0.003 N(2)* −0.039

interplanar angle between (1) and (2): 92.0°
(2) and (3): 169.2

*Atoms excluded in the calculation of the least-squares plane.

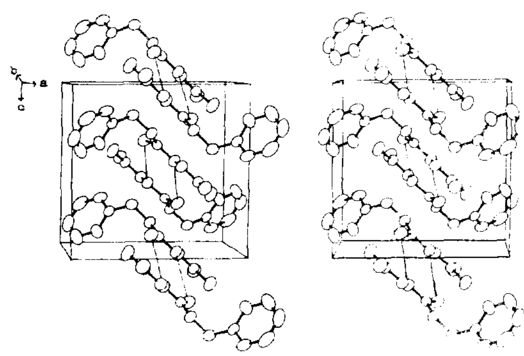


Fig. 3. Molecular packing and hydrogen bonding in acetone 4-benzylthiosemicarbaone viewed down the *b* axis. The *a* axis is horizontal. Thin solid lines are hydrogen bonds.

an NH_2 group in eight thiosemicarbazones[1,4~9] while for N(2), we have an NH attached to another nitrogen atom. In addition, the most reasonable resonance forms for the thiosemicarbazones have greater double bond character in the C(8)-N(1) bond. The valence angles around C(8) are also different. The average S-C(8)-N(1) bond angle of 124(1)° is significantly greater than the average S-C(8)-N(2) bond angle of 119(1)°.

In most of the thiosemicarbazone derivatives, *trans* S-C(8)-N(2)-N(3) arrangement is adopted with only one exception, *i.e.*, salicylaldehyde 4-piperidinothiosemicarbazone[11]; there is an intramolecular hydrogen bond between N(3) and OH of the salicyl group. Therefore, it has been assumed that the preferred conformation was determined by the steric repulsion between S and N(3) atoms and the probable intramolecular hydrogen bond between N(1)H and N(3) atoms.

The conformations around C(9)-N(3) bond are similar in both ABTC and ATC molecules. Atoms of N(2), N(3), C(9), C(10) and C(11) are coplanar within an experimental error (*Table* 5). This planar conformation seems to be due to conjugation of Pπ electron on the C(9) atom with N(2) and N(3) atoms. The important conformational angles are given in *Table* 4.

The least-squares planes are listed in *Table* 5. The benzene ring is planar within an experimental error. The formylthiosemicarbazone group is also planar and perpendicular to the benzene ring plane with an interplanar angle of 92.0°. Acetone thiosemicarbazone part of the molecule is coplanar within ±0.159Å and C(4) atom is 1.185Å out of the plane.

Table 6. Hydrogen bonds and close contacts (less than 3.7Å) of acetone 4-benzylthiosemicarbazone

(A) Hydrogen bonds				
D-H...A	D-H	H...A	D...A	D-H...A
N(2)-H...S[a]	0.76Å	2.82Å	3.555Å	165°
N(1)-H...N(3)	0.85	2.09	2.568	116
(B) Close contacts				
S...C(11)[a]			3.471	
N(2)...C(7)[b]			3.572	
N(3)...C(7)[b]			3.589	
C(11)...C(1)[c]			3.587	
C(9)...N(1)[b]			3.651	
C(4)...C(10)[d]			3.644	

Symmetry code
[a] $1-x$, $2-y$, $1-z$; [b] x, $1/2-y$, $-1/2+z$; [c] $-1+x$, $1/2-y$, $-1/2+z$; [d] $1-x$, $1-y$, $1-z$

The molecular packing is illustrated in ***Fig.*** 3 and the probable hydrogen bonds are tabulated in *Table* 6. Acetone 4-benzylthiosemicarbazone has two hydrogen atoms capable of hydrogen bonding. N(2)H forms hydrogen bond to S with the N(2)...S length of 3.555Å. The N(2)H...S hydrogen bonds which are between two molecules related by a center of symmetry at (1/2, 1, 1/2) make dimer-like molecules. The geometry of the N(2)H...S hydrogen bond is typical of the hydrogen bonds found in other thiosemicarbazone crystals. N(1)H does not involve intermolecular hydrogen bond but does remain in the best position for intramolecular hydrogen bonding to N(3).

The benzene groups are packed together along the two-fold screw axis. The contacts between the planes involve only van der Waals forces. There are six intermolecular contacts less than 3.7Å. The closest contact occur between S and C(11) with distance of 3.47Å.

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