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Structural studies of N(4)-substituted thiosemicarbazones prepared from 4-formylantipyrine and a thiourea derived from 4-aminoantipyrine

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Reaction of 4-formylantipyrine with $N(4)$-dimethylthiosemicarbazide and 3-piperidylthiosemicarbazide produces the $N(4)$-dimethylthiosemicarbazone (**1**), and the 3-piperidylthiosemicarbazone (**2**), respectively. Compound **1** is triclinic, space group P-1 with $a = 6.329(1)$ Å, $b = 11.699(1)$ Å, $c = 11.943(1)$ Å, $\alpha = 65.83(1)^\circ$, $\beta = 80.83(1)^\circ$, $\gamma = 84.90(1)^\circ$, and $V = 796.1(1)$ Å^3 with $Z = 2$, for $D_{\text{calc}} = 1.324$ g/cm^3. Compound **2** is triclinic, space group P-1 with $a = 6.784(1)$ Å, $b = 10.485(2)$ Å, $c = 13.462(3)$ Å, $\alpha = 102.05(2)^\circ$, $\beta = 98.61(2)^\circ$, $\gamma = 101.32(2)^\circ$, and $V = 899.8(5)$ Å^3 with $Z = 2$, for $D_{\text{calc}} = 1.319$ g/cm^3. Reaction of 4-aminoantipyrine with phenyl isothiocyanate produced N-antipyrine-N'-phenylthiourea (**3**). Compound **3** is monoclinic, space group $P2_1/n$ with $a = 6.863(7)$ Å, $b = 15.361(3)$ Å, $c = 16.332(5)$ Å, $\beta = 90.35(6)^\circ$, and $V = 1720.7(18)$ Å^3 with $Z = 4$, for $D_{\text{calc}} = 1.306$ g/cm^3. Compounds **1** and **2** have intermolecular hydrogen bonding between the carbonyl oxygen of the antipyrine moiety and the NH hydrogen of the thiosemicarbazone moiety. In **3** the two unique molecules are held together as a dimer by interactions of the two thiourea NH's and the antipyrine moiety's oxygen.

KEY WORDS: Antipyrine; thiosemicarbazone; thiourea; hydrogen bonding; planarity.

Introduction

Antipyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) and its derivatives possess a wide variety of potentially useful biological properties,[1] and thiosemicarbazones and thioureas have demonstrated significant antitumor activity.[2] The activity of thiosemicarbazones has been shown to be significantly affected by substitution at the moiety's N(4)-position.[3] Although there have been a number of studies on 2-formylpyridine thiosemicarbazones,[4,5] only recently have the spectral properties of 4-formylantipyrine thiosemicarbazones and their metal complexes been reported.[6–10] Here we report the crystal structures of the $N(4)$-dimethylthiosemicarbazone (**1**) and 3-piperidylthiosemicarbazone (**2**) of

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4-formylantipyrine, as well as *N*-4-antipyrine-*N*′-phenylthiourea (**3**).

Experimental

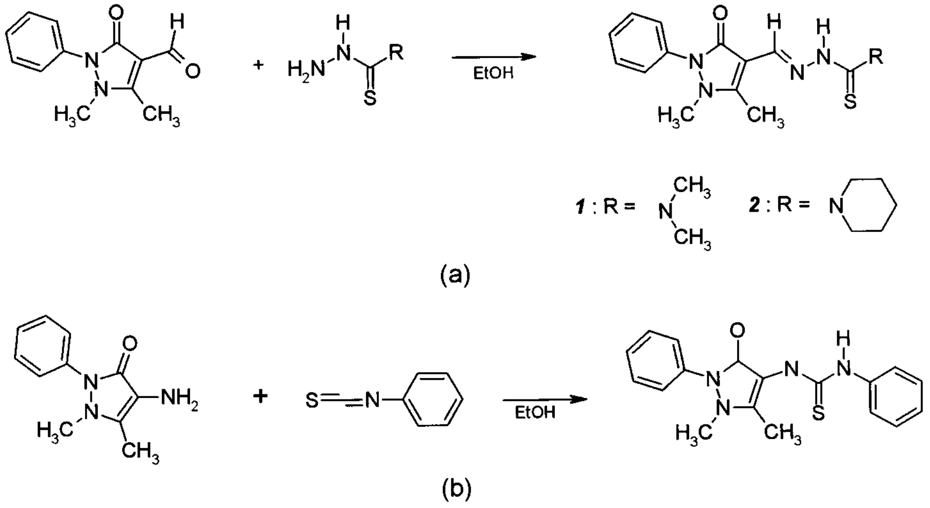
N(4)-dimethyl- and 3-piperidylthiosemicarbazide were prepared by the method described by Scovill.[11] The thiosemicarbazones were prepared by refluxing a 1:1 molar mixture of 4-formylantipyrine (Aldrich) and the desired thiosemicarbazide in absolute ethanol with two drops of concentrated H_2SO_4 added as reported previously.[6] Compound **3** (mp 206–207°C) was prepared by mixing 4-aminoantipyrine (Aldrich) and phenyl isothiocyanate (Aldrich) in 95% ethanol with gentle warming. On slow evaporation a beige solid separated and was isolated by suction filtration.

The crystals were grown by slow evaporation of ethanol solutions and mounted in random orientation on glass fibers. Reflections for **1**, **2**, and **3** were acquired with Siemens P4, Nicolet P3/F, and Nonius MACH3 diffractometers, respectively. Crystal stability was monitored using three standard reflections every 97 reflections. The structures were solved by direct methods,[12] missing atoms were found by difference Fourier synthesis, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters with SHELX-97.[13] Hydrogens attached to nitrogens were found on a difference Fourier map and refined isotropically while hydrogens attached to carbons were located in their calculated positions, and refined using a riding model. Scattering factors are from the International Tables for Crystallography (1974, Vol IV)[14] for **1** and **2** and Wassmaire and Kirfel[15] for **3**. The graphics used are PLATON.[16]

Results

The thiosemicarbazones **1** and **2**, were prepared by condensation of 4-formylantipyrine and the desired thiosemicarbazide, Scheme 1(a). The thiourea, **3**, was synthesized from 4-aminoantipyrine and phenyl isothiocyanate as shown in Scheme 1(b).

Table 1 summarizes the crystal data, collection information, and refinement data for the three antipyrine derivatives, and Table 2 lists the atomic coordinates and equivalent isotropic displacement coefficients. Selected bond distances and angles are shown in Table 3, bond distances and angles



Scheme 1. Procedure for the synthesis of (a) the thiosemicarbazones **1** and **2** and (b) the thoiurea **3**.

Table 1. Crystallographic Data and Methods of Data Collection, Solution and Refinement for **1**, **2**, and **3**

	1	**2**	**3**
CCDC no.	CCDC 171822	CCDC 171823	CCDC 171821
Color; habit	Yellow; prism	Yellow; prism	Beige, prism
Empirical formula	$C_{15}H_{19}N_5OS$	$C_{18}H_{23}N_5OS$	$C_{18}H_{18}N_4OS$
Formula weight	317.4	357.5	338.42
Temperature, K	293(2)	293(2)	293(2)
Crystal size, mm	0.40 × 0.12 × 0.10	0.40 × 0.24 × 0.08	0.30 × 0.26 × 0.14
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/n$
Unit cell dimensions			
a, Å	6.329(1)	6.784(1)	6.863(7)
b, Å	11.699(1)	10.485(2)	15.361(3)
c, Å	11.943(1)	13.462(3)	16.332(5)
α, deg	65.83(1)	102.05(2)	90
β, deg	80.83(1)	98.61(2)	90.35(6)
γ, deg	84.90(1)	101.32(2)	90
Volume, Å^3	796.1(1)	899.8(5)	1720.7
Z	2	2	4
Density (calculated), Mg/m^3	1.324	1.319	1.306
Absorption coefficient mm^{-1}	1.884	1.727	0.200
F (000)	336	380	712
Radiation, λ (Å)	Cu Kα, 1.54178	Cu Kα, 1.54178	Mo Kα, 0.71073
θ range for data collection, deg	1.5–55.0	1.5–55.0	2.49–24.66
Index ranges	$0 \leq h \leq 6$ $-11 \leq k \leq 11$ $-12 \leq l \leq 12$	$0 \leq h \leq 7$ $-11 \leq k \leq 10$ $-14 \leq l \leq 14$	$0 \leq h \leq 8$ $0 \leq k \leq 18$ $-19 \leq l \leq 19$
Reflections collected	2146	2496	3282
Independent reflections, R_{int}	1930, 0.0543	2262, 0.0468	3022
Observed reflections, $F > 3.0\sigma(F)$	1630	2065	1843, 0.0221
Absorption correction	Face-indexed numerical	Ψ-scan	Ψ-scan
Min./max. transmission	0.7738/0.866	0.6291/0.8705	0.8410/1.0000
Extinction correction		0.024(4)	0.0052(8)
Final R indices (observed data)	$R = 0.0672$, $wR = 0.0971$	$R = 0.0454$, $wR = 0.0746$	$R = 0.0557$, $wR = 0.1001$
R indices (all data)	$R = 0.0796$, $wR = 0.1189$	$R = 0.0487$, $wR = 0.0771$	$R = 0.1277$, $wR = 0.1390$
Goodness of fit	1.54	1.53	1.174
Data to parameter ratio	8.0:1	8.98:1	6.47:1
Largest diff. peak/hole	0.36/−0.37	0.31/−0.31	0.348/−0.330

for **3** have been arranged so that they correspond to the analogous bonds of **1** and **2**. The molecular geometries, thermal ellipsoids (30%), and numbering schemes are shown in Figs. 1–3.

In the crystal structure of **1**, the sulfur atom and the imine nitrogen (N3) are *syn* with respect to C7—N4, as shown in Fig. 1. The phenyl ring is essentially perpendicular and the mean plane of the thiosemicarbazone moiety is almost coplanar with the pyrazole ring. Neighboring molecules form dimers held together by two N—H $\cdots$ O hydrogen bonds involving the thiosemicarbazone N4 and O1 (N1—O1 = 2.971(4) Å).

In the crystal structure of **2,** the sulfur and the imine nitrogen are *anti* with respect to C7—N4, Fig. 2. The angle between the mean plane of phenyl ring and the mean plane of the pyrazole ring is ca. 63°, and the angle between the mean planes of the thiosemicarbazone moiety and the pyrazole ring is ca. 13°. Neighboring molecules form dimers held together by two N—H $\cdots$ O hydrogen bonds involving the thiosemicarbazone N4 and O1 (N $\cdots$ O = 3.066(3) Å).

Two unique molecules are present in the asymmetric unit of **3**. The two unique molecules interact through N—H $\cdots$ O hydrogen bonds,

Table 2. Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^{2}x10^3) for **1**, **2**, and **3**

	x	*y*	*z*	U_{eq}
1				
S1	3460(2)	2687(1)	9622(1)	66(1)
O1	−3354(6)	789(3)	15467(3)	64(2)
N1	−4912(7)	3364(4)	12973(3)	55(2)
N2	−5333(6)	2434(4)	14196(3)	53(2)
N3	1003(6)	1715(4)	12069(3)	55(2)
N4	2906(6)	1076(4)	11986(3)	52(2)
N5	6053(7)	846(4)	10860(3)	58(2)
C3	−3574(8)	1617(4)	14424(4)	50(2)
C4	−2190(7)	1976(4)	13274(4)	45(2)
C5	−3084(8)	3031(4)	12430(4)	48(2)
C6	−183(8)	1340(4)	13103(4)	48(2)
C7	4220(8)	1477(4)	10876(4)	46(2)
C8	6680(9)	−240(5)	11928(5)	65(2)
C9	7585(10)	1165(6)	9745(5)	74(3)
C10	−2344(9)	3777(5)	11084(4)	61(2)
C11	−6661(9)	4147(5)	12392(5)	64(2)
C12	−6755(8)	2740(4)	15094(4)	48(2)
C13	−8803(9)	2278(6)	15459(4)	68(3)
C14	−10156(10)	2587(7)	16320(6)	89(3)
C15	−9542(14)	3343(7)	16800(6)	95(3)
C16	−7499(14)	3799(6)	16453(5)	90(3)
C17	−6101(10)	3493(5)	15601(5)	68(2)
2				
S1	1762(1)	14(1)	6146(1)	59(1)
O1	−63(3)	−1332(2)	11113(1)	48(1)
N1	3628(3)	−3189(2)	11134(2)	45(1)
N2	2145(3)	−2627(2)	11575(2)	44(1)
N3	3153(3)	−1241(2)	8601(2)	41(1)
N4	2794(3)	−411(2)	7958(2)	45(1)
N5	4724(4)	−1171(2)	6745(2)	49(1)
C3	1393(4)	−1855(2)	10960(2)	38(1)
C4	2584(3)	−1853(2)	10164(2)	38(1)
C5	3931(4)	−2653(3)	10319(2)	40(1)
C6	2303(4)	−1110(2)	9393(2)	41(1)
C7	3213(4)	−578(2)	6981(2)	43(1)
C8	5059(5)	−1483(3)	5675(2)	57(1)
C9	5348(5)	−2892(3)	5381(2)	61(1)
C10	7035(5)	−3126(3)	6132(2)	68(1)
C11	6725(5)	−2717(3)	7231(2)	59(1)
C12	6452(4)	−1301(3)	7477(2)	49(1)
C13	5579(4)	−2949(3)	9743(2)	54(1)
C14	5273(4)	−3413(3)	11870(2)	54(1)
C15	1077(4)	−3289(2)	12228(2)	40(1)
C16	874(4)	−2551(3)	13155(2)	49(1)
C17	−157(5)	−3176(3)	13794(2)	61(1)
C18	−943(4)	−4526(3)	13513(3)	63(1)
C19	−759(4)	−5267(3)	12586(3)	62(1)
C20	254(4)	−4657(3)	11930(2)	54(1)
3				
C13	6879(12)	2773(6)	6606(5)	40(2)
C14	7780(12)	1940(5)	6643(5)	40(2)
C15	9690(12)	2044(6)	6433(5)	47(2)
C16	6376(11)	501(6)	6409(5)	47(2)
C17	4432(12)	−872(6)	6468(5)	45(2)
C18	2494(12)	−1070(6)	6638(5)	54(2)
C19	1690(16)	−1833(7)	6362(7)	76(3)
C20	2745(14)	−2404(7)	5889(6)	65(3)
C21	4638(16)	−2214(6)	5706(6)	68(3)
C22	5496(14)	−1443(6)	5999(5)	60(2)
C23	1.1393(11)	3205(7)	5666(6)	63(3)
C24	8249(13)	4280(6)	6411(6)	47(2)
C25	9414(15)	4708(7)	6960(7)	77(3)
C26	9300(17)	5612(8)	6975(9)	102(4)
C27	8094(18)	6045(7)	6453(9)	94(4)
C28	6929(17)	5599(8)	5933(8)	84(3)
C29	6986(15)	4709(6)	5895(7)	67(3)
C30	11247(12)	1376(7)	6361(6)	65(3)
C33	2451(13)	1250(6)	8475(5)	46(2)
C34	1762(12)	2118(6)	8485(5)	44(2)
C35	−147(12)	2104(6)	8724(5)	45(2)
C36	3342(13)	3540(6)	8618(5)	50(2)
C37	4938(13)	4970(6)	8399(6)	51(2).
C38	6071(15)	5124(7)	9067(6)	72(3)
C39	6572(16)	5974(8)	9254(7)	75(3)
C40	5957(17)	6645(7)	8798(7)	73(3)
C41	4873(19)	6497(8)	8113(9)	90(4)
C42	4329(14)	5660(6)	7900(7)	69(3)
C43	−1985(12)	1053(7)	9576(6)	66(3)
C44	758(13)	−160(6)	8687(5)	48(2)
C45	−903(15)	−516(7)	8336(6)	60(3)
C46	−1145(18)	−1385(7)	8243(6)	75(3)
C47	34(2)	−1941(8)	8498(7)	93(4)
C48	2010(19)	−1592(7)	8843(7)	78(3)
C49	2195(15)	−717(6)	8930(6)	58(3)
C50	−1558(13)	2830(7)	8807(6)	68(3)
N11	10048(9)	2909(5)	6302(5)	492(19)
N12	8280(10)	3343(5)	6353(4)	493(19)
N13	6773(10)	1191(5)	6902(4)	473(19)
N14	5193(9)	−96(5)	6791(4)	438(18)
N31	−0710(9)	1268(5)	8884(4)	487(18)
N32	947(10)	738(5)	8777(4)	476(18)
N33	2852(11)	2828(5)	8175(4)	494(19)
N34	4356(12)	4124(5)	8152(5)	56(2)
O11	5127(7)	3005(4)	6768(3)	477(15)
O31	4046(8)	942(4)	8218(4)	533(17)
S11	7247(4)	400	54637(15)	643(8)
S31	2769(4)	3673(2)	95939(16)	725(9)

involving N13 and N14 ($N \cdots O = 2.883(9)$ and 2.934(9) Å, respectively) and N33 and N34 ($N \cdots O = 2.798(9)$ and 2.89(1) Å, respectively) to form a dimer, as shown in Fig. 3. There are no significant differences in the bond distances and angles of the two different molecules. The greatest difference between the two unique molecules of **3** is

Table 3. Selected Bond Distances (Å) and Angles (°) for **1**, **2**, and **3**

	1	**2**		**3**	
Bond					
S1—C7	1.689(4)	1.680(3)	S11—C16	1.666(8)	1.656(9)[a]
O1—C3	1.246(5)	1.243(3)	O11—C13	1.283(9)	1.267(9)
N1—N2	1.419(4)	1.406(3)	N11—N12	1.387(9)	1.410(9)
N1—C5	1.341(6)	1.357(4)	N11—C15	1.37(1)	1.37(1)
N1—C11(C14)	1.446(7)	1.467(4)	N11—C23	1.47(1)	1.47(1)
N2—C3	1.386(6)	1.385(4)	N12—C13	1.37(1)	1.39(1)
N2—C12(C15)	1.427(6)	1.424(4)	N12—C24	1.44(1)	1.39(1)
N3—N4	1.372(6)	1.379(3)			
N3—C6	1.266(5)	1.282(3)			
N4—C7	1.370(5)	1.370(4)	N13—C16	1.36(1)	1.35(1)
N5—C7	1.321(6)	1.343(4)	N14—C16	1.38(1)	1.37(1)
N5—C8	1.463(6)	1.471(4)	N14—C17	1.40(1)	1.42(1)
N5—C9(C12)	1.449(3)	1.462(4)			
C5—C10(C13)	1.499(6)	1.497(4)	C15—C30	1.49(1)	1.48(1)
Angles					
N2—N1—C5	107.8(3)	107.0(2)	N12—N11—C15	107.4(6)	106.8(6)
N2—N1—C11(C14)	119.2(4)	115.6(2)	N12—N11—C23	116.6(7)	116.8(7)
C5—N1—C11(C14)	128.3(4)	124.2(2)	C15—N11—C23	121.8(7)	121.9(7)
N1—N2—C3	108.1(3)	109.1(2)	N11—N12—C13	109.1(7)	108.6(7)
N1—N2—C12(C15)	118.9(4)	118.8(2)	N11—N12—C24	119.8(7)	120.6(7)
C3—N2—C12(C15)	126.2(4)	126.3(2)	C13—N12—C24	127.5(7)	126.3(8)
N4—N3—C6	117.7(3)	115.5(2)			
N3—N4—C7	118.5(3)	123.9(2)	C14—N13—C16	123.9(7)	124.2(7)
C7—N5—C8	123.8(4)	120.8(2)	C16—N14—C17	128.0(8)	125.9(8)
C7—N5—C9(C12)	121.5(4)	126.5(2)			
O1—C3—N2	123.1(4)	123.1(2)	O11—C13—N12	123.1(8)	123.4(8)
O1—C3—C4	130.8(4)	130.8(3)	O11—C13—C14	130.5(7)	130.2(8)
N2—C3—C4	106.0(3)	106.0(2)	N12—C13—C14	106.4(7)	106.3(7)
C3—C4—C5	107.7(4)	107.1(2)	C13—C14—N13	122.3(7)	122.9(7)
C3—C4—C6	123.8(3)	122.4(2)	C13—C14—C15	107.6(7)	108.0(8)
C5—C4—C6	128.5(4)	130.5(2)	C15—C14—N13	130.1(8)	128.4(8)
N1—C5—C4	109.9(3)	110.4(2)	N11—C15—C14	109.1(7)	110.0(7)
N3—C6—C4	121.1(4)	122.9(3)	N11—C15—C30	121.8(8)	120.2(7)
S1—C7—N4	120.7(3)	115.9(2)	S11—C16—N13	123.4(7)	123.7(7)
S1—C7—N5	123.5(3)	124.0(2)	S11—C16—N14	124.9(7)	125.3(7)
N4—C7—N5	115.8(3)	120.1(2)	N13—C16—N14	111.7(7)	111.0(7)

[a] The number in this column is the analogous bond in the S31 molecule.

in their planarity. For example, the mean plane of the phenyl ring in the S11 molecule has an angle of 38.2(3)° to the mean plane of the pyrazole ring, but is at an angle of 72.9(3)° in the S31 molecule.

Discussion

The bond distances of the thiosemicarbazone and pyrazolone moieties in the thiosemicarbazones **1** and **2** are similar; the distance of the N5—C7 bond is most different as might be expected due to the different functional groups attached to N5. The N5—C7 bond is considerably shorter than the N4—C7 bond indicating some restriction of rotation in the former. In **3** the bond distances in the pyrazole ring are similar to those of the thiosemicarbazones, but the C13—O11 bond is marginally longer. In addition, the thione bond, C16—S11, is marginally shorter indicating less delocalization of electron density in **3**. In contrast to bond distances,

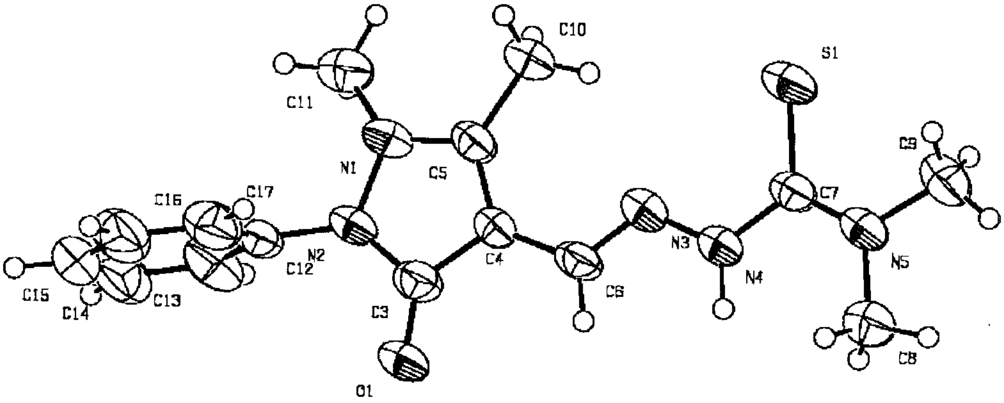


Fig. 1. A view of the two unique molecules of **3** with the atomic numbering scheme, showing the intermolecular hydrogen bonding interactions. Thermal ellipsoids are drawn at the 30% probability level.

the bond angles of the thiosemicarbazone moieties show significant differences. In particular, N3—N4—C7, S1—C7—N4, and N4—C7—N5 are different by more than 4°. These differences in bond angles result from the size requirements of the piperidyl ring compared to the methyl groups of **1**. There are also significant differences for the two molecules in the bond angles involving the *N*-methyl function of the pyrazolone moiety; both N2—N1—C11(C14) and C5—N1—C11(C14) differ by about 4°. One of the angles in the pyrazolone moiety that shows a significant difference between the two thiosemicarbazones, C5—N1—C11, is also signficantly different for **3** (i.e., C15—N11—C21 and C35—N31—C41), other comparable angles are similar.

Considering the angles between mean planes of the phenyl ring, the thiosemicarbazone and the pyrazole ring, the smaller thiosemicarbazone **1** is the more planar. Compared to **1** and **2**, **3** is considerably less planar consistent with the more unsaturated nature of the thiosemicarbazone moiety compared to the thiourea moiety.

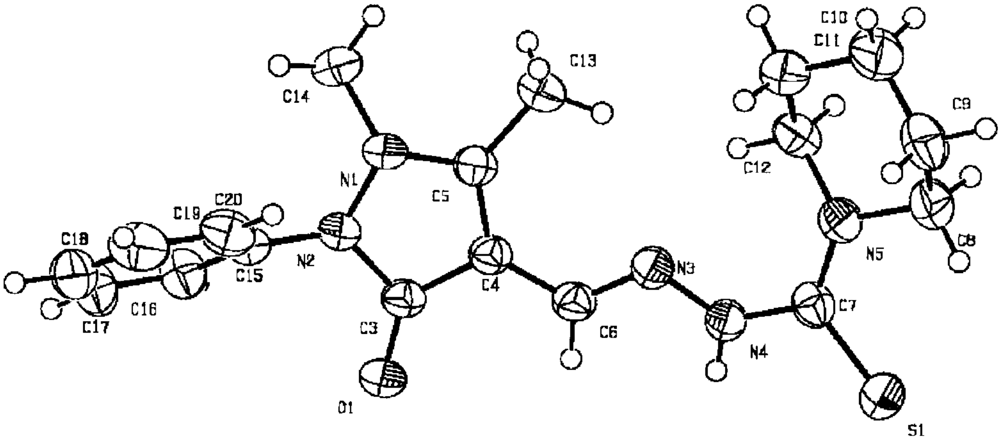


Fig. 2. A view of **1** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

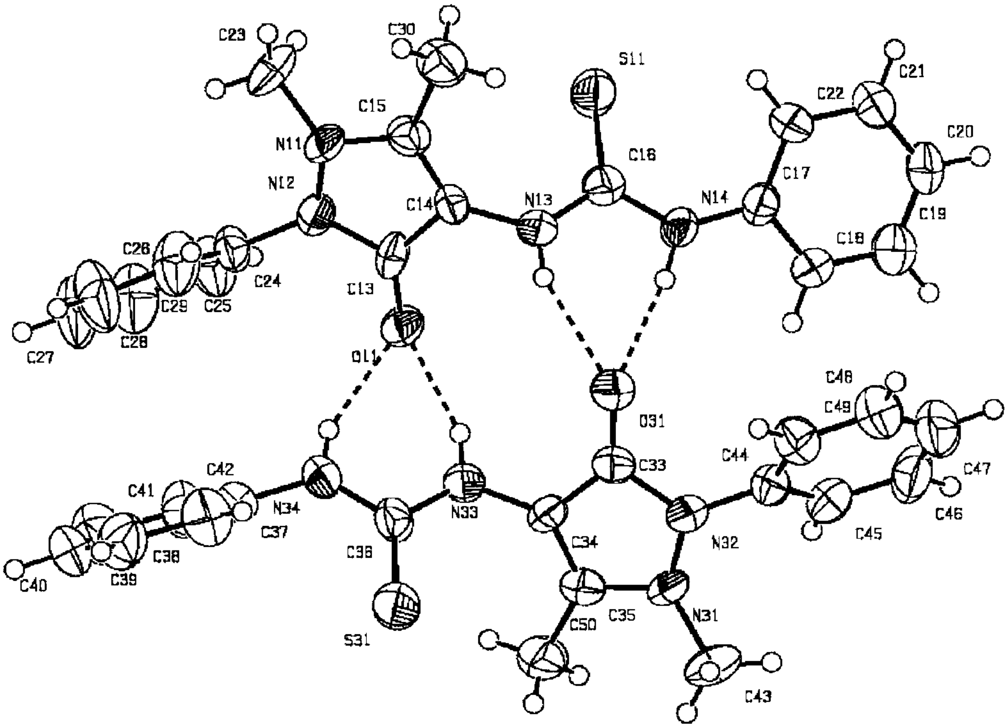


Fig. 3. A view of **2** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

In thiosemicarbazones the hydrogen attached to N4 is often involved in weak intramolecular hydrogen bonding [5,17–19]. However, in these two thiosemicarbazones formation of a 7-membered ring (i.e., N4—H4—O1—C3—C4—C6—N3) is less favorable than intermolecular N4—H4 · · · O1 hydrogen bonds.

We have presented the structural information for two N(4)-substituted thiosemicarbazones prepared with 4-formylantipyrine and a thiourea prepared from 4-aminoantipyrine. Therefore, since biological testing of both thioureas[20] and thiosemicarbazones[21] is being carried out in many laboratories, these compounds represent new series that can be tested and a structure/activity relationship can be determined.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 171822 for **1**, CCDC 171823 for **2**, and CCDC 171821 for **3**. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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