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Journal of Molecular Structure 522 (2000) 27–36

Journal of
MOLECULAR
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Structural and spectral studies of *N*-2-(4,6-lutidyl)-*N*′-tolylthioureas

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Received 6 May 1999; accepted 21 June 1999

Abstract

N-2-(4,6-lutidyl)-*N*′-*o*-tolylthiourea, 4,6LuTuoT, triclinic, *P-1*, $a = 7.470(2)$, $b = 9.799(5)$, $c = 10.269(3)$ Å, $\alpha = 90.514(4)$, $\beta = 98.89(3)$, $\gamma = 90.14(3)°$, $V = 742.5(9)$ Å^3, $Z = 2$, $\mu = 2.09\ \text{mm}^{-1}$; *N*-2-(4,6-lutidyl)-*N*′-*m*-tolylthiourea, 4,6LuTumT, monoclinic, *P2₁/a*, $a = 7.2393(2)$, $b = 16.636(3)$, $c = 12.557(1)$ Å, $\beta = 101.968(9)°$, $V = 1479.4(6)$ Å^3, $Z = 4$, $\mu = 2.10\ \text{mm}^{-1}$ and *N*-2-(4,6-lutidyl)-*N*′-*p*-tolylthiourea, 4,6LuTupT, triclinic, *P-1*, $a = 7.883(2)$, $b = 7.9024(8)$, $c = 23.273(4)$ Å, $\alpha = 86.49(1)$, $\beta = 86.48(2)$, $\gamma = 88.45(2)°$, $V = 1443.9(7)$ Å^3, $Z = 4$, $\mu = 2.15\ \text{mm}^{-1}$. These molecules have an intramolecular hydrogen bond between N′H and the pyridyl nitrogen, as well as intermolecular hydrogen bonding between NH and a thione sulfur of a second molecule to form centrosymmetric dimers. Solution ^{1}H NMR studies ($CDCl_3$) show the N′H resonance considerably downfield for each thiourea and its position, as well as that of NH, are affected by substituents on the phenyl ring. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heterocyclic thioureas; Hydrogen bonding; Crystal structure

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1. Introduction

Although representative heterocyclic thioureas have been shown to be biologically potent compounds [1] and several thiourea derivatives have been characterized as prospective agents for antiviral chemotherapy [2], their structures, and in particular, the various modes of hydrogen bonding have received little attention. ^{1}H NMR correctly predicted intramolecular hydrogen bonding between the pyridyl nitrogen and N′H in 2-pyridyl thioureas [3], but only recently a structural study has been reported for *N*-(2-pyridyl)-*N*′-phenylthiourea [4]. Studies of a number of substituted thioureas including *N*-benzoyl-*N*′-thioureas indicate an intramolecular hydrogen bond between N′H and oxygen (i.e. benzoyl, etc.) [5–10]. There is also a weak intermolecular N2H hydrogen bond with a sulfur of a neighboring molecule to form a two-dimensional (2D) network in these latter thioureas. In addition, crystal structures of substituted thioureas with intermolecular hydrogen bonding, but without intramolecular hydrogen bonding, have been reported [11–15]. More recent studies of substituted *N*-(2-pyridyl)-*N*′-phenylthioureas including *N*-2-(4,6-lutidyl)-*N*′-phenylthiourea, 4,6LuTuPh [16] and *N*-(2-pyridyl)-*N*′-tolylthioureas have been reported [17]. Here we report the crystal structures and lattice arrangements for thioureas having methyl groups situated on both the pyridyl ring (i.e. 4,6-lutidyl derivatives) and the aromatic ring (i.e. tolyl derivatives), Fig. 1, which possess both intramolecular and intermolecular hydrogen bonding.

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PII: S0022-2860(99)00314-2

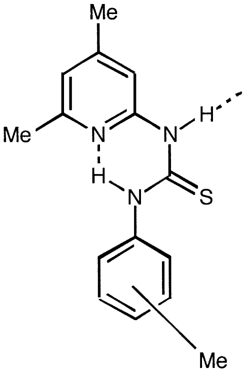

Fig. 1. A representation of a *N*-(4,6-lutidyl)-*N*′-tolylthiourea showing expected intramolecular and intermolecular hydrogen bonding.

2. Experimental

4,6-Dimethyl-2-aminopyridine was purchased from Aldrich and used as received. It was mixed in a 1:1 molar ratio with *o*-tolyl-, *m*-tolyl- or *p*-tolylisothiocyanate (Aldrich) in 95% ethanol, and the resulting mixture gently refluxed for a minimum of 1 h. On cooling and slowly evaporating (35°C) the reactant mixture, the thioureas crystallized from solution. They were filtered, washed with cold isopropanol followed by anhydrous ether, dried on a warm plate and then stored until required for characterization. The yields are ca. 65% for each of the thioureas and the melting points are as follows: 4,6LuTuoT, 180–182°C; 4,6LuTumT, 184–186°C; and 4,6LuTupT, 202–204°C. Their ^{1}H NMR spectra were recorded in $CDCl_3$ with a Varian Gemini 2000 300 MHz spectrometer. IR spectra were recorded as nujol mulls between NaCl plates with a Nicolet 5SCX FT Spectrometer and UV spectra with a Cary 5E spectrophotometer in 1 cm cells.

Colorless, prismatic crystals of the thioureas were grown by slow evaporation of acetone–ethanol solutions (1:1 by volume) at room temperature. The structures were solved with direct methods and missing atoms were found by difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic temperature factors and all hydrogens were found on the difference Fourier map. The H atoms of CH were allowed to ride on the C atoms and assigned fixed isotropic temperature factor, $U = 0.05$ Å^2. Only the coordinates of the H atoms attached to N and N′ were refined. Refinement of the structures was made by full-matrix least-squares. Scattering factors are from Wassmaire and Kirfel [18], calculations were done by maXus, version 2.0 [19] and graphics are Platon for Windows [20].

3. Results and discussion

3.1. Structural studies

The crystallographic data and methods of data collection, solution and refinement for 4,6LuTuoT, 4,6LuTumT and 4,6LuTupT are shown in Table 1 and the atomic coordinates and equivalent isotropic displacement coefficients are included in the deposited material (CCDC), as are a complete list of bond distances and angles. The CCDC(s are as follows: $4,6\mathrm{LuTuoT} = 118\,645$, $4,6\mathrm{LuTumT} = 118\,646$ and $4,6\mathrm{LuTupT} = 118\,655$.

The molecular structures of the three 4,6-lutidyl thioureas are represented by 4,6LuTumT in Fig. 2, the intermolecular and intramolecular hydrogen bonding by 4,6LuTuoT in Fig. 3 and the packing common to the three by 4,6LuTupT in Fig. 4. All three are in a conformation resulting from intramolecular hydrogen bonding of N′H to the pyridine nitrogen, N1, in a manner similar to the benzoyl thioureas and *trans–cis* like *N*-cyclohexyl-*N*′-phenylthiourea [14]. Inspection of Table 2 shows that the bond distances for the three 2-lutidyl thioureas are generally within three orders of magnitude of their estimated standard deviations. The largest difference is found in the N3–C8 bonds as might be expected because of the change in position of the methyl group on the aromatic ring. The bond angles do show some variation; the angles involving the tolyl ring bonding to N3 show the greatest variation. For example, C7–N3–C8 is 125.6(2), 128.7(3) and averages 133.1(3)° for 4,6LuTuoT, 4,6LuTumT and 4,6LuTupT, respectively. Thus, the position (i.e. *ortho, meta* or *para*) of the methyl group on the aryl ring has an effect on the bonding of the thiourea moiety in these lutidyl derivatives, but an effect of this magnitude was not found for the *N*-(2-pyridyl)-*N*′-tolyl thioureas [17].

Table 3 shows bond distances and angles for 4,6LuTuoT, 4,6LuTumT and 4,6LuTupT along with

Table 1
Crystallographic data and methods of data collection, solution and refinement for 4,6LuTuoT, 4,6LuTumT and 4,6LuTupT

	4,6LuTuoT	4,6LuTumT	4,6LuTupT
Crystal data			
Empirical formula	$C_{15}H_{17}N_3S$	$C_{15}H_{17}N_3S$	$C_{15}H_{17}N_3S$
Crystal color, habit	Colorless, prism	Colorless, prism	Colorless, prism
Crystal size (mm)	$0.32 \times 0.28 \times 0.20$	$0.30 \times 0.26 \times 0.18$	$0.40 \times 0.14 \times 0.12$
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/a$	P-1
a (Å)	7.470(2)	7.2393(8)	7.883(2)
b (Å)	9.799(5)	16.636(3)	7.9024(8)
c (Å)	10.269(3)	12.557(1)	23.273(4)
α (°)	90.514(4)	90(0)	86.49(1)
β (°)	98.89(3)	101.968(9)	86.48(2)
γ (°)	90.14(3)	90(0)	88.45(2)
V (Å^3)	742.5(9)	1479.4(6)	1443.9(7)
Z	2	4	4
Formula weight	271.4	271.4	271.4
Density (calcd.) (g/cm^3)	1.214	1.219	1.248
Absorption coefficient (mm^{-1})	2.09	2.10	2.15
$F(000)$	288	576	576
Data collection			
Diffractometer	Nonius Mach 3	Nonius Mach 3	Nonius Mach 3
Radiation (wavelength, Å)	MoK$_\alpha$ (0.70930)	MoK$_\alpha$ (0.70930)	MoK$_\alpha$ (0.70930)
Temperature (K)	293	293	293
Monochromator	Highly oriented graphite crystal	Highly oriented graphite crystal	Highly oriented graphite crystal
2θ range (°)	2.0–55.0	2.0–55.0	2.0–55.0
Scan type	ω/θ	ω/θ	ω/θ
Scan range (ω,°)	0.80	0.80	0.80
Index ranges	$0 \leq h \leq 9$	$0 \leq h \leq 9$	$0 \leq h \leq 10$
	$-12 \leq k \leq 12$	$0 \leq k \leq 21$	$-10 \leq k \leq 10$
	$-13 \leq l \leq 13$	$-16 \leq l \leq 16$	$-30 \leq l \leq 30$
Reflections collected	3811	3934	7387
Ind. Reflec.(R_{int} %)	3673 (2.29)	3658 (1.77)	7089 (3.096)
Observed reflections	2983 ($I > 3.0\sigma(I)$)	2644 ($I > 3.0\sigma(I)$)	4577 ($I > 3.0\sigma(I)$)
Absorption correction	ψ-Scan	ψ-Scan	ψ-Scan
Maximum and minimum transmissions	1.000 and 0.984	1.000 and 0.956	1.000 and 0.966
Solution and refinement			
Solution method	Direct methods	Direct methods	Direct methods
Goodness-of-fit	0.578	1.076	0.915
Data/parameter ratio	16.8:1	15.4:1	13.3:1
Largest diff. Peak (eÅ^{-3})	0.60	0.50	0.31
Largest diff. Hole (eÅ^{-3})	− 0.24	− 0.31	− 0.37
R	0.045	0.051	0.052
ωR	0.094	0.1881	0.1038
Programs used	maXus	maXus	maXus

other 2-pyridylthioureas, and includes representative N,N'-substituted thioureas that do not have intramolecular hydrogen bonding [11–15]. Previously [16], it was found that the only significant differences between the pyridyl thioureas and the previously studied thioureas (i.e. benzoyl, etc.) that have intramolecular hydrogen bonding, N3–H···O is that the pyridyl thioureas have shorter N2–C7 bonds and the C7–S1 bond is marginally longer. Since the 2-pyridyl thioureas do not have an electron withdrawing carbonyl group attached to N, the N–C7 bond has slightly more double bond character. Also, there is

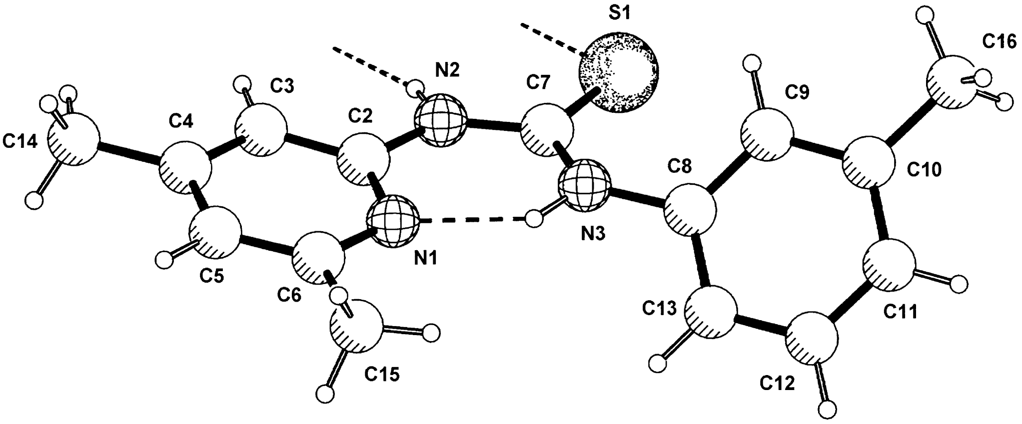

Fig. 2. A perspective view of 4,6LuTumT showing intramolecular hydrogen bonding.

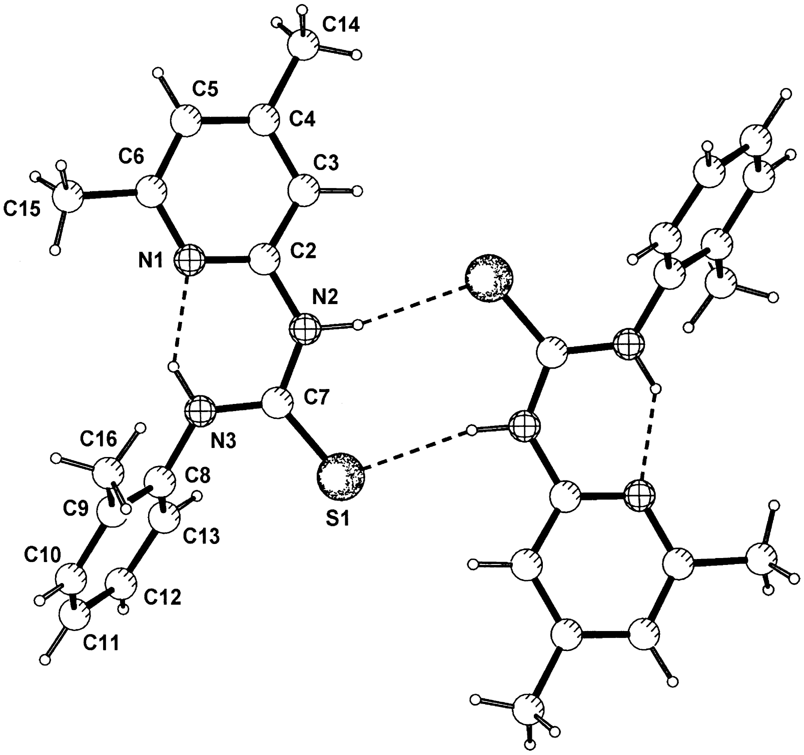

Fig. 3. A perspective view of 4,6LuTuoT showing both intramolecular and intermolecular hydrogen bonding and the molecule's lack of planarity.

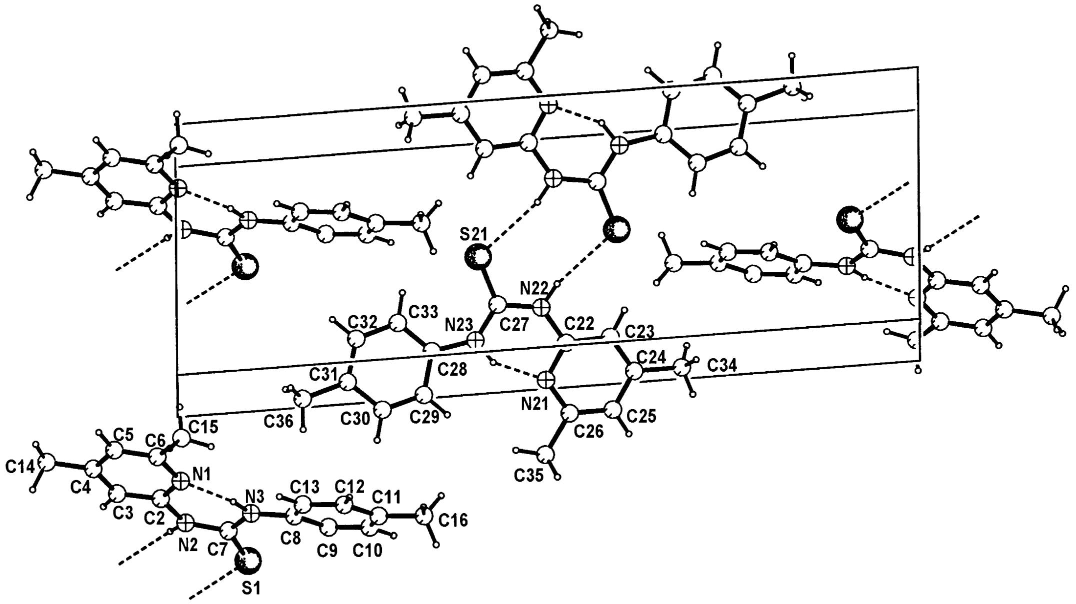

Fig. 4. A unit cell of 4,6LuTupT showing the mode of packing of the dimers, both intramolecular and intermolecular hydrogen bonding and the molecule's nearly planar structure.

Table 2
Selected bond distances (Å) and angles (°) for 4,6LuTuoT, 4,6LuTumT and 4,6LuTupT

	4,6LuTuoT	4,6LuTumT	4,6LuTupT[a]
Bond distances (Å)			
S1–C7	1.687(3)	1.691(4)	1.686(4) 1.690(4)
N1–C2	1.337(3)	1.337(4)	1.334(5) 1.335(5)
N1–C6	1.349(3)	1.360(4)	1.353(5) 1.350(5)
N2–C2	1.402(4)	1.411(4)	1.408(5) 1.415(5)
N2–C7	1.370(4)	1.374(5)	1.382(5) 1.364(5)
N3–C7	1.339(4)	1.339(5)	1.332(5) 1.344(5)
N3–C8	1.436(4)	1.431(5)	1.421(5) 1.413(5)
Bond angles (°)			
C2–N2–C7	129.2(3)	129.8(3)	129.7(3) 130.1(3)
C7–N3–C8	125.6(2)	128.7(3)	132.9(3) 133.4(3)
N1–C2–N2	118.4(3)	118.3(3)	118.2(3) 118.0(3)
N2–C2–C3	118.3(3)	117.9(3)	118.4(3) 118.6(3)
S1–C7–N2	119.1(2)	118.3(3)	117.5(3) 118.0(3)
S1–C7–N3	124.1(2)	125.6(3)	127.1(3) 126.3(3)
N2–C7–N3	116.9(2)	116.2(3)	115.4(3) 115.8(3)
N3–C8–C9	118.6(3)	121.8(4)	114.7(3) 115.0(3)
N3–C8–C13	119.8(3)	116.6(4)	126.5(4) 126.2(4)

[a] The second values represent the analogous bonds in the second molecule.

no significant difference in the thiourea moiety's bond angles between the present thioureas and those previously studied [5–9]. In general, the two thioureas included in Table 3 that have only intermolecular hydrogen bonding, PhTuPh [11] and Me$_2$TuoT [13], show the following differences from thioureas with intramolecular hydrogen bonding: the N–C7 bond is shorter, N–C7–S1 angle larger and the N′–C7–S1 angle smaller. There are no significant differences in the bond distances and angles among the nine 2-pyridyl thioureas shown in Table 3.

Shown in Table 4 are the three hydrogen bonding interactions found for the 2-pyridyl thioureas. The intramolecular N3–H3···N1 hydrogen bonding shows a wide range of non-bonding N3–H3···N1 distances. For unsubstituted PyTuPh this distance is 2.646(4) Å, but substitution on the pyridyl ring strengthens this bonding, reducing the distance to an average of 2.608(4) for the two forms of 4,6LuTupT and to 2.626(4) and 2.629(4) Å for 4,6LuTumT and 4,6LuTuPh, respectively. However, ortho substitution on the aryl ring weakens this interaction so that 4,6LuTuoT has a N3–H3···N1 distance of 2.667(3) Å and PyTuoT, a distance of 2.687(4) Å. An even longer distance (average of the two forms)

Table 3
Selected bond distances (Å) and bond angles (°) for substituted thioureas

Compound	Bond distances (Å)			Bond angles (°)			Reference
	N2–C7	S1–C7	N3–C7	N2–C7–N3	N2–C7–S1	N3–C7–S1	
BzOTupNO$_2$Ph[a]	1.393(3)	1.658(2)	1.344(3)	115.0(2)	118.3(2)	126.6(2)	[6]
BzOTupMeOPh[b]	1.392(4)	1.659(3)	1.329(4)	115.4(3)	119.2(2)	125.4(2)	[7]
PhTuPh[c]	1.349(4)	1.681(5)	1.349(4)	113.9(4)	123.0(2)	123.0(2)	[9]
Me$_2$TuoT[d]	1.356(4)	1.693(3)	1.337(4)	115.6(3)	121.5(3)	122.9(2)	[11]
PyTuPh[e]	1.374(4)	1.682(3)	1.335(4)	116.8(5)	118.6(4)	124.6(4)	[2]
PyTuoT[f]	1.370(4)	1.678(3)	1.336(4)	116.9(4)	119.7(4)	123.4(4)	[15]
PyTumT[g]	1.377(3)	1.684(2)	1.331(3)	116.7(2)	118.8(2)	123.5(2)	[15]
	1.373(3)	1.684(2)	1.334(3)	117.9(2)	118.4(2)	123.7(2)	
PyTupT[h]	1.373(4)	1.684(4)	1.324(6)	116.0(3)	118.6(3)	125.4(2)	[15]
	1.378(6)	1.672(4)	1.354(6)	116.4(7)	119.0(6)	124.5(6)	
6PiTuPh[i]	1.375(4)	1.679(3)	1.333(4)	115.8(5)	117.3(4)	126.9(4)	[14]
4,6LuTuPh[j]	1.366(4)	1.689(3)	1.341(4)	115.5(2)	117.6(2)	126.9(2)	[14]
4,6LuTuoT	1.370(4)	1.687(3)	1.339(4)	116.9(2)	119.1(2)	124.1(2)	[k]
4,6LuTumT	1.374(5)	1.691(4)	1.339(5)	116.2(3)	118.3(3)	125.6(3)	[k]
4,6LuTupT	1.382(5)	1.686(4)	1.332(5)	115.4(3)	117.5(3)	127.1(3)	[k]
	1.364(5)	1.690(4)	1.344(5)	115.8(3)	118.0(3)	126.3(3)	

[a] *N*-benzoyl-*N*′-(4-nitrophenyl)thiourea.
[b] *N*-benzoyl-*N*′-(4-methoxyphenyl)-thiourea.
[c] *N*,*N*′-diphenylthiourea.
[d] *N*-dimethyl-*N*′-*o*-tolylthiourea.
[e] *N*-(2-pyridyl)-*N*′-phenylthiourea.
[f] *N*-2-pyridyl-*N*′-*o*-tolylthiourea.
[g] *N*-2-pyridyl-*N*′-*m*-tolylthiourea.
[h] *N*-2-pyridyl-*N*′-*p*-tolylthiourea.
[i] *N*-6-methyl-2-pyridyl-*N*′-phenylthiourea.
[j] *N*-4,6-dimethyl-2-pyridyl-*N*′-phenylthiourea.
[k] This work.

has been found for PyTumT, 2.698(3) Å. Similar variation occurs in the H3···N1 distances shown in Table 4. The N3–H3···N1 bond angles range from an average of 132(2)° for PyTumT to 150(3) for 4,6LuTuPh. Therefore, substitution in the 4-position of the pyridyl ring strengthens this intramolecular hydrogen bonding and substitution in the 6-position of the pyridyl ring has little effect since 6-PiTuPh and PyTuPh have similar N3–H3···N1 distances. Substitution on the para-position of the aryl ring also strengthens this bonding, but substituting the ortho- and meta-positions weakens intramolecular hydrogen bonding.

As was found for *N*-benzoyl-*N*′-(4-methoxyphenyl)thiourea [10], N2H̲ in the present thioureas and the previously studied 2-pyridyl thioureas [4,16,17] is involved in intermolecular hydrogen bonding with a sulfur from a neighboring molecule, Table 4. This results in centrosymmetric dimer formation. The N2–H2···SA non-bonding distance for PyTuPh is 3.412(3) Å and shorter distances are found for PyTuoT, 3.401(2) Å and 4,6LuTuoT, 3.348(3) Å, as well as 6PiTuPh, 3.383(3) Å. Therefore, substitution on the aryl ring strengthens this interaction, and substitution on the pyridyl ring strengthens it to an even greater extent. Weakening this intermolecular interaction is substitution at the *para*-position of the aryl ring since PyTupT and 4,6LuTupT have average non-bonding N2–H2···SA distances of 3.437(4) and 3.474(3) Å, respectively. The bond angles range from an average of 156(2)° for PyTumT to 169(4)° for PyTupT.

In addition to the N–H···S hydrogen bond, the thioureas' sulfur is also interacting with a pyridyl hydrogen, C3H. The non-bonding distances and angles are also included in Table 3. The C3–H···S

Table 4
Intramolecular and intermolecular hydrogen bond distances (Å) and angles (°) for the various *N*(2-pyridyl)-*N′*-arylthioureas

Thiourea	H3···N1 (Å)	N3-H3···N1 (Å)	∠N3–H3···N1 (°)
Intramolecular			
PyTuPh	1.96(3)	2.646(4)	133(2)
PyTuoT	1.944(4)	2.687(4)	140(3)
PyTumT	2.262(2) 1.941(2)	2.701(3) 2.696(3)	129(2) 134(2)
PyTupT	1.93(4) 1.95(4)	2.646(4) 2.665(4)	140(5) 137(3)
6PiTuPh	1.82(3)	2.645(4)	144(2)
4,6LuTuPh	1.76(4)	2.629(4)	150(3)
4,6LuTuoT	1.896(2)	2.667(3)	141(2)
4,6LuTumT	1.840(3)	2.626(4)	143(2)
4,6LuTupT	1.784(3) 1.801(3)	2.605(4) 2.611(4)	148(2) 146(2)
Intermolecular			
	H2···SA (Å)	N2–H2···SA (Å)	∠N2–H2···SA (°)
PyTuPh	2.55(3)	3.412(3)	163(2)
PyTuoT	2.45(2)	3.401(2)	159(2)
PyTumT	2.51(1) 2.49(1)	3.407(2) 3.380(3)	157(2) 155(2)
PyTupT	2.47(5) 2.68(5)	3.352(4) 3.523(4)	167(4) 171(4)
6PiTuPh	2.45(3)	3.383(3)	168(2)
4,6LuTuPh	2.66(4)	3.461(2)	165(3)
4,6LuTuoT	2.482(1)	3.348(3)	158.0(2)
4,6LuTumT	2.534(1)	3.428(3)	165.8(2)
4,6LuTupT	2.573(1) 2.612(1)	3.469(3) 3.480(3)	166.4(2) 158.3(2)
	C3H···SA (Å)	C3–H···SA (Å)	∠C3–H···SA (°)
PyTuPh	2.81	3.643(4)	146
PyTuoT	2.84	3.619(3)	138
PyTumT	2.78 2.84	3.566(3) 3.643(3)	140 142
PyTupT	2.70 2.96	3.528(5) 3.801(5)	146 147
6PiTuPh	2.85	3.656(3)	142
4,6LuTuPh	2.89	3.706(3)	143
4,6LuTuoT	2.98	3.660(3)	129
4,6LuTumT	2.96	3.724(4)	138
4,6LuTupT	2.81 2.82	3.643(4) 3.650(4)	145 146

Table 5
Angles between mean planes of the various *N*-(2-pyridyl)-*N′*-arylthioureas[a]

Compound	∠plane A/plane B	∠plane B/plane C	∠plane A/plane C
PyTuPh	5.4(1)	58.0(1)	63.2(1)
PyTuoT	13.6(2)	75.5(1)	67.4(1)
PyTumT	4.6(1) 2.08(4)	76.1(1) 77.2(1)	80.2(1) 78.6(1)
PyTupT	10.2(1) 2.1(1)	55.5(1) 56.5(1)	58.8(1) 58.6(1)
6PiTuPh	3.89(3)	11.17(6)	11.2(7)
4,6LuTuPh	4.66(3)	13.23(6)	13.9(9)
4,6LuTuoT	19.2(4)	68.0(4)	64.1(3)
4,6LuTumT	4.9(4)	46.7(4)	45.2(3)
4,6LuTupT	3.1(4) 3.3(4)	16.7(4) 16.7(4)	18.3(3) 18.3(3)

[a] Plane A: mean plane of pyridine ring, plane B: mean plane of the thiourea moiety, N–C(S)–N′ and plane C: mean plane of the aromatic ring.

Table 6
^{1}H, ^{13}C NMR (δ), ultraviolet and infrared spectral date for *N*-(2-pyridyl)-*N*′-arylthioureas

Compound	N′ H	NH	C=S	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	ν(C=S)	ν(NH)	Reference
PyTuPh[a]	13.865	10.903	178.7	37040 (4.298)[b]	32900 (4.429)	857 m	3195 m	[14]
PyTuoT	13.494	10.013	179.3	37040 (4.226)	32890 (4.358)	850 m	3200 m	[15]
PyTumT	13.644	9.401	178.7	33980 sh	32350 (4.382)	831 m	3185 m	[15]
PyTupT	13.771	10.031	178.8	37040 (4.278)	32890 (4.391)	818 m	3200 m	[15]
6MTuPh[c]	14.103	9.205	178.0	37040 (4.319)	32470 (4.468)	850 m	3197 m	[14]
4,6MTuPh[d]	14.119	8.311	178.1	37040 (4.264)	32680 (4.443)	828 m	3205 m	[14]
4,6MTuoT	13.689	9.318	179.3	34590 sh	32790 (4.488)	845 s	3172 sh	[e]
4,6MTumT	14.052	8.731	178.4	34470 sh	32670 (4.468)	831 m	3200 m	[e]
4,6MTupT	14.067	9.159	178.4	34470 sh	32670 (4.497)	818 m	3214 m	[e]

[a] *N*-2-pyridyl-*N*′-phenylthiourea.
[b] log ϵ.
[c] *N*-6-methyl-2-pyridyl-*N*′-phenylthiourea.
[d] *N*-4,6-dimethyl-2-pyridyl-*N*′-phenylthiourea.
[e] This work.

distance for PhTuPy is 3.643(4) Å and substitution on the pyridyl ring weakens this interaction (e.g. 6PiTuPh, 3.656(3) Å and 4,6LuTuPh, 3.706(3) Å), but substitution on the aryl ring appears to strengthen this bonding (e.g. PyTuoT, 3.619(3) Å). The non-bonding C3–H···S angles range from 129 to 146°.

Each of the 4,6-lutidyl thioureas has a very planar thiourea moiety with no atom deviating from the plane by more than 0.0040 Å. Table 5 lists the dihedral angles between the pyridyl ring and the thiourea moiety planes, the thiourea moiety and the aryl ring planes and the pyridyl and aryl ring planes. The angles between the planes should be useful in interpreting the differences in the hydrogen bonding interactions discussed earlier. For the intramolecular hydrogen bond, N3–H3···N1, the dihedral angle between the pyridyl and aryl ring planes reflects the strongest and weakest bonding. That is, 4,6LuTupT, which has the shortest N3–H3···N1 distance, has an pyridyl/aryl ring angle of 18.3(3)° for its two forms and PyTumT, which has the longest N3–H3···N1 distance, has an angle of 79.4(1)°. The pyridyl ring/thiourea bond angles show a similar trend. 4,6LuTuoT has the shortest N2–H2···SA non-bonding distance and the largest pyridyl ring/thiourea moiety dihedral angle, 19.2(4)° this angle averages 3.2(4)° for 4,6LuTupT, which has one of the longer N2–H2···SA distances. When all three angles are considered, 6PiTuPh has the most planar structure and features about average N3–H3···N1, somewhat shorter N2–H2···SA and longer C3–H···SA non-bonding distances.

Although the bond distances and angles among the nine 2-pyridyl thioureas studied to date do not show significant variation, the distances and angles involved in the three hydrogen bonding interactions do have considerable variation. The dihedral angles between the mean plane of the thiourea moiety and the pyridyl and aryl mean planes result from differences in solid state packing due to the various positions of the methyl groups on the two rings.

3.2. Spectral studies

The UV spectra (DMSO) show a single band with a high energy shoulder for 4,6LuTuoT, 4,6LuTumT and

4,6LuTupT, and one or two bands for the six other 2-pyridyl thioureas reported previously [16,17], (Table 6) which we assign to a combination of $\pi \rightarrow \pi^*$ transitions from both rings and an $n \rightarrow \pi^*$ of the heterocyclic ring. Other bands involving the thiourea function are evidently obscured by this latter band. In the infrared spectra of 4,6LuTuoT, 4,6LuTumT and 4,6LuTupT, ν(N2H) is assigned to a medium intensity absorption band at ca. $3200\ \mathrm{cm}^{-1}$ and ν(CS) to bands between 800 and $860\ \mathrm{cm}^{-1}$ range in agreement with the six previously studied thiosemicarbazones [16,17].

The ^{1}H NMR spectra show some variation in the shift of the N3$\underline{\mathrm{H}}$ resonance due to differences in the intramolecular hydrogen bonding in the nine pyridyl thioureas studied to date. Addition of methyl groups to the pyridyl ring provides greater electron density to the pyridine nitrogen causing a downfield shift for the resonance of N3$\underline{\mathrm{H}}$. In contrast, the *o*-methyl group in PyTuoT and 4,6LuTuoT weakens the intramolecular N3H3$\cdots$N1 interaction based on the upfield position for N3$\underline{\mathrm{H}}$ compared to the other thioureas in Table 6. This is presumably due to these molecules' less planar arrangement, which also occurs in the solid state as discussed earlier. There is a significant upfield shift for the resonance assigned to N2$\underline{\mathrm{H}}$ due to methyl groups on the pyridyl ring; methyl groups on the phenyl ring also cause an upfield shift, but of smaller magnitude. Thus, the inductive effect of the methyl groups enriches the electron density in the NH bond, and the more remote methyl groups on the phenyl ring do so to a lesser extent. However, none of the nine thioureas shows a significant difference in the ^{13}C resonance of $\underline{\mathrm{C}}$S with differing numbers of methyl groups on either ring. Thus, like the structural parameters, the spectral data are generally very similar for the nine *N*-(2-pyridyl)-*N'*-arylthioureas studied to date; the greatest difference involves the chemical shifts of the two N$\underline{\mathrm{H}}$s.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/m. Copies of available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: + 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation and the Consejo Nacional de Ciencia y Tecnologia for the partial support of this research.

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