

Structural, spectral and thermal studies of substituted *N*-(2-pyridyl)-*N'*-phenylthioureas

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Abstract

N-2-(3-picolyl)-*N'*-phenylthiourea, 3PicTuPh, monoclinic, $P2_1/n$, $a = 7.617(2)$, $b = 7.197(5)$, $c = 22.889(5)$ Å, $\beta = 94.63(4)^\circ$, $V = 1250.7(1)$ Å³ and $Z = 4$; *N*-2-(4-picolyl)-*N'*-phenylthiourea, 4PicTuPh, triclinic, $P-1$, $a = 7.3960(5)$, $b = 7.9660(12)$, $c = 21.600(3)$ Å, $\alpha = 86.401(4)$, $\beta = 84.899(8)$, $\gamma = 77.769(8)^\circ$, $V = 1237.5(3)$ Å³ and $Z = 4$; *N*-2-(5-picolyl)-*N'*-phenylthiourea, 5PicTuPh, monoclinic, $P2_1/c$, $a = 14.201(1)$, $b = 4.905(3)$, $c = 17.689(3)$ Å, $\beta = 91.38(1)^\circ$, $V = 1231.8(7)$ Å³ and $Z = 4$; *N*-2-(6-picolyl)-*N'*-phenylthiourea, 6PicTuPh, monoclinic, $C2/c2$, $a = 14.713(1)$, $b = 9.367(1)$, $c = 18.227(1)$ Å, $\beta = 92.88(1)^\circ$, $V = 2515.5(1)$ Å³ and $Z = 8$ and *N*-2-(4,6-lutidyl)-*N'*-phenylthiourea, 4,6LutTuPh, monoclinic, $C2/c$, $a = 11.107(2)$, $b = 11.793(2)$, $c = 20.084(4)$ Å, $\beta = 96.10(3)^\circ$, $V = 2616(1)$ Å³ and $Z = 8$. Intramolecular hydrogen bonding between *N'*H and the pyridyl nitrogen and intermolecular hydrogen bonding involving the thione sulfur are affected by substitution of the pyridine ring, as is the planarity of the molecule. ¹H NMR studies in CDCl₃ show the NH' hydrogen resonance considerably downfield from other resonances in the spectrum for each thiourea. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2-Pyridyl thioureas; Crystal structures; Hydrogen bonding; Plane deviation

1. Introduction

The structure of *N*-(2-pyridyl)-*N'*-phenylthiourea [1] has been reported following a ¹H NMR study of the intramolecular hydrogen bonding between the pyridyl nitrogen and *N'*H for *N*-(2-pyridyl)thioureas [2]. Studies of a number of substituted thioureas,

including *N*-benzoylthioureas, show intramolecular hydrogen bonding between *N'*H and the benzoyl, alkyl or acyl oxygen [3–10]. There is also an intermolecular NH hydrogen bond with a sulfur of a neighboring molecule to form a two-dimensional network in these latter thioureas. In addition, crystal structures of substituted thioureas with intermolecular N–H⋯S bonding, but without intramolecular hydrogen bonding, have been reported [11–15]. More recent structural studies of substituted *N*-(2-pyridyl)-*N'*-arylthioureas include *N*-(2-pyridyl)-*N'*-tolylthioureas

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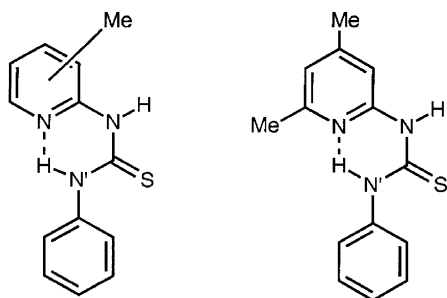


Fig. 1. Representations of *N*-picolyl- and *N*-4,6-lutidyl-*N'*-phenylthioureas with expected intramolecular hydrogen bonding.

[16], the three *N*-2-(4,6-lutidyl)-*N'*-tolylthioureas [17], *N*-(5-bromo-2-pyridyl)-*N'*-2-(2,5-dimethoxyphenylethyl)thiourea [18] and four thioureas with *p*-substituted aryl groups, *N*-(2-pyridyl)-*N'*-4-bromophenyl-, *N*-(2-pyridyl)-*N'*-4-chlorophenyl-, *N*-(2-pyridyl)-*N'*-4-methoxyphenyl- and *N*-(2-pyridyl)-*N'*-4-nitrophenylthioureas [19]. The aforementioned 2-pyridyl thioureas, like *N*-benzoyl-*N'*-thioureas [3–10], feature both intramolecular and intermolecular hydrogen bonding, but ring substituents affect the distances and angles of both types of hydrogen bonds. A recent communication showed that some members of a series of *N*-(2-pyridyl)-*N'*-2-methoxyphenylthioureas possess bifurcated intramolecular hydrogen bonding to the pyridyl nitrogen and methoxy oxygen [20]. We prepared and acquired crystals of the *N*-2-(picolyl)-*N'*-phenylthioureas and *N*-(4,6-lutidyl)-*N'*-phenylthiourea in order to determine whether methyl groups at various positions on the pyridyl ring alter the nature or strength of the hydrogen bonding interactions, as well as the overall planarity of the molecule. The ^1H and ^{13}C NMR spectra have been recorded for each of the thioureas, which are represented in Fig. 1.

2. Experimental

2-amino-3-picoline, 2-amino-4-picoline, 2-amino-5-picoline, 2-amino-6-picoline and 2-amino-4,6-lutidine were purchased from Aldrich and used as received. Phenyl isothiocyanate (Aldrich) was mixed in a 1:1 molar ratio with the desired substituted pyridine in 95% ethanol and the mixture stirred with warming for a minimum of 1 h. On cooling and slowly

evaporating the reactant mixture (35 °C), the thioureas crystallized from solution. The solids were filtered, washed with cold isopropanol, dried on a warm plate and then stored until required for spectral characterization. The yields are ca. 75% for each of the thioureas and the melting points are as follows: 3PicTuPh, 122–4 °C; 4PicTuPh, 160–161 °C; 5PicTuPh, 179–180 °C; 6PicTuPh, 187–188 °C; and 4,6LutTuPh, 216–217 °C. Their ^1H NMR spectra were recorded in CDCl_3 with a Varian Gemini 2000 300 MHz spectrometer. Infrared and ultraviolet spectra were recorded with Perkin–Elmer 783 and Hewlett Packard 8452 A Diode Array spectrophotometers, respectively.

Crystals of the five thioureas were grown by slow evaporation of 1:1 by volume acetone–anhydrous ethanolic mixtures at room temperature. The colorless thiourea crystals were mounted in random orientation on a glass fiber on a Nonius MACH3 Four Circle Diffractometer (3PicTuPh), Nonius Kappa CCD Diffractometer (4PicTuPh, 5PicTuPh), Siemens P4 (6PicTuPh) and Siemens P3/F (4,6LutTuPh) Four Circle Diffractometers. The structures were solved by direct methods and missing atoms were found by difference-Fourier synthesis. The non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogens were found on a difference Fourier map. For all the thioureas except 4PicTuPh and the pyridine ring of 5PicTuPh the hydrogens attached to carbons were allowed to ride on their carbons and assigned fixed isotropic displacement parameters, $U = 0.05 \text{ \AA}^2$. For 4PicTuPh, the methyl hydrogens were allowed to ride in a disordered model, but the other hydrogens were refined isotropically as were the hydrogens on the pyridine ring of 5PicTuPh. The coordinates of the H atoms attached to nitrogen in each of the thioureas were refined isotropically. The two phenyl ring positions in 5PicTuPh are ca. 60° from each other with equal occupancy. For 3PicTuPh, scattering factors are from Wassmaier and Kirfel [21], calculations were done by maXus, version 2.0 [22,23], and graphics are PLATON for Windows [24]. For 4PicTuPh and 5PicTuPh DENZO [25] was used for data reduction, scattering factors are from Wassmaier and Kirfel [21], structure refinement by SHELXL-97 and graphics are ZORTEP [26]. For 6PicTuPh and 4,6LutTuPh scattering factors were taken from International Tables for X-ray

Table 1
Crystal data, summary of data collection and structure refinement for 3PicTuPh, 4PicTuPh, 5PicTuPh, 6PicTuPh and 4,6LuTuPh

Compound	3PicTuPh	4PicTuPh	5PicTuPh	6PicTuPh	4,6LuTuPh
Color/shape	Colorless/prism	Colorless/prism	Colorless/needle	Colorless/prism	Colorless/prism
Empirical formula	C ₁₃ H ₁₃ N ₃ S	C ₁₃ H ₁₃ N ₃ S	C ₁₃ H ₁₃ N ₃ S	C ₁₃ H ₁₃ N ₃ S	C ₁₄ H ₁₅ N ₃ S
Formula weight	243.3	243.3	243.3	243.3	257.4
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> ₂ / <i>m</i> (#14)	<i>P</i> -1(#2)	<i>P</i> ₂ / <i>c</i> (#14)	<i>C</i> ₂ / <i>c</i> (#15)	<i>C</i> ₂ / <i>c</i> (#15)
Unit cell dimensions					
<i>a</i> (Å)	7.617(5)	7.3960(5)	14.201(1)	14.713(1)	11.107(2)
<i>b</i> (Å)	7.197(2)	7.9660(12)	4.905(3)	9.367(1)	11.793(2)
<i>c</i> (Å)	22.889(5)	21.600(3)	17.689(3)	18.227(1)	20.084(4)
α (°)	90	86.401(4)	90	90	90
β (°)	94.63(4)	84.899(8)	91.38(1)	92.88(1)	96.10(3)
γ (°)	90	77.769(8)	90	90	90
Volume (Å ³)	1250.7(9)	1237.5(3)	1231.8(7)	2515.5(1)	2616(1)
Z, Density (calcd) (mg/m ³)	4, 1.292	4, 1.306	4, 1.312	8, 1.285	8, 1.307
Absorption coefficient (mm ⁻¹)	0.239	0.242	0.243	2.12	2.067
Radiation/wavelength (Å)	Mo K α /0.71073	Mo K α /0.71073	Mo K α /0.71073	Cu K α /1.54178	Cu K α 1.54178
<i>F</i> (000)	512	512	512	1024	1088
Crystal size (mm)	0.20 × 0.18 × 0.15	0.29 × 0.17 × 0.15	0.75 × 0.10 × 0.07/c >	0.36 × 0.30 × 0.20	0.28 × 0.28 × 0.20
θ range for data collection (°)	2.89–27.47	1.89–24.66	2.30–24.73	1.5–25.0	1.5–25.0
Index ranges	0 ≤ <i>h</i> ≤ 9	−8 ≤ <i>h</i> ≤ 7	−13 ≤ <i>h</i> ≤ 16	0 ≤ <i>h</i> ≤ 15	−11 ≤ <i>h</i> ≤ 11
	−9 ≤ <i>k</i> ≤ 9	−9 ≤ <i>k</i> ≤ 7	−4 ≤ <i>k</i> ≤ 5	0 ≤ <i>k</i> ≤ 9	0 ≤ <i>k</i> ≤ 12
	−29 ≤ <i>l</i> ≤ 29	−21 ≤ <i>l</i> ≤ 28	−20 ≤ <i>l</i> ≤ 16	−19 ≤ <i>l</i> ≤ 19	0 ≤ <i>l</i> ≤ 21
Reflections collected	4476	5931	5432	1643	1649
Independent reflections (<i>R</i> _{int})	2709, 0.0195	3878, 0.0504	1996, 0.0687	1572, 0.0336	1649, 0.000
Observed reflections	1785 { <i>I</i> > 2 σ (<i>I</i>)}	1702 { <i>I</i> > 2 σ (<i>I</i>)}	1193 { <i>I</i> > 2 σ (<i>I</i>)}	1358 { <i>F</i> ² > 4 σ (<i>F</i> ²)}	1487 { <i>F</i> ² > 4 σ (<i>F</i> ²)}
Absorption correction	Ψ -scans	HKL Scalepack	HKL Scalepack	Semi-empirical	Difabs
Goodness-of-fit	1.109	0.865	0.982	1.08	1.042
Final <i>R</i> indices	<i>R</i> = 0.0480	<i>R</i> = 0.0444	<i>R</i> = 0.0479	<i>R</i> = 0.0535	<i>R</i> = 0.0472
	<i>wR</i> = 0.1103	<i>wR</i> = 0.0810	<i>wR</i> = 0.1069	<i>wR</i> ₂ = 0.1334	<i>wR</i> ₂ = 0.1264
<i>R</i> indices (all data)	<i>R</i> = 0.0821	<i>R</i> = 0.1370	<i>R</i> = 0.0958	<i>R</i> = 0.0605	<i>R</i> = 0.0508
	<i>wR</i> = 0.1373	<i>wR</i> = 0.1039	<i>wR</i> = 0.1238	<i>wR</i> ₂ = 0.1402	<i>wR</i> ₂ = 0.1334
Largest diff. peak/hole (e Å ⁻³)	0.362/−0.275	0.147/−0.167	0.180/−0.181	0.266/−0.214	0.316/−0.336
Data/parameter ratio	13.9:1	10.0:1	9.4:1	9.7:1	9.7:1

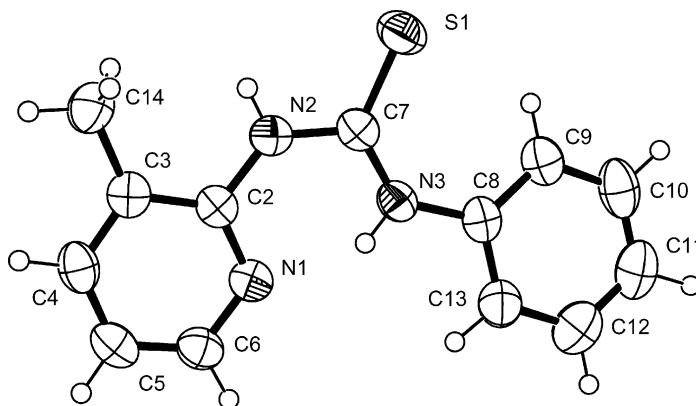


Fig. 2. Thermal ellipsoid plot showing 3PicTuPh with atom numbering scheme and displacement ellipsoids at 50% probability level.

Crystallography (1974, Vol. IV) [27] and calculations were done with the SHELXTL PC™ program package [28]. Table 1 summarizes the crystal data, collection information and refinement statistics for these thioureas.

3. Results and discussion

3.1. Structural studies

The ORTEP diagrams of 3PicTuPh, 4PicTuPh, 5PicTuPh, 6PicTuPh and 4,6LutTuPh, as well as a packing diagram of 4,6LutTuPh, representing the

five thioureas of this study, are shown in Figs. 2–7. 3PicTuPh, 5PicTuPh, 6PicTuPh and 4,6LutTuPh crystallize with one unique molecule in the cell, but 4PicTuPh has two crystallographic unique molecules per unit cell. These thioureas, like other pyridyl thioureas [1,16–20], are found in a conformation resulting from intramolecular hydrogen bonding of $N3H(N'H)$ to the pyridine nitrogen, N1, in a manner similar to the benzoyl and acyl thioureas [3–10] and *cis-cis* like *N*-phenyl-*N'*-phenylthiourea [11]. The five thioureas have similar bond distances and angles, Table 2, and the only notable difference is the C2–N1–C6 angle, which may be due to different positions of the methyl groups and/or differences in hydrogen

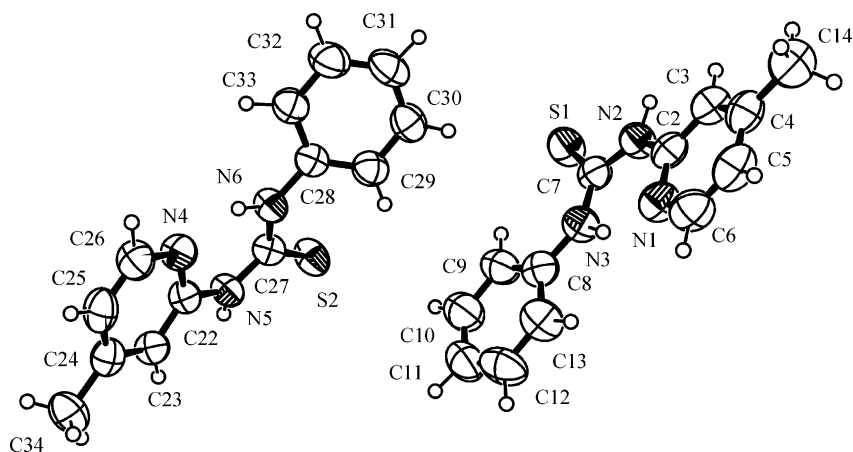


Fig. 3. Thermal ellipsoid plot showing the two unique molecules of 4PicTuPh with atom numbering scheme and displacement ellipsoids at 50% probability level.

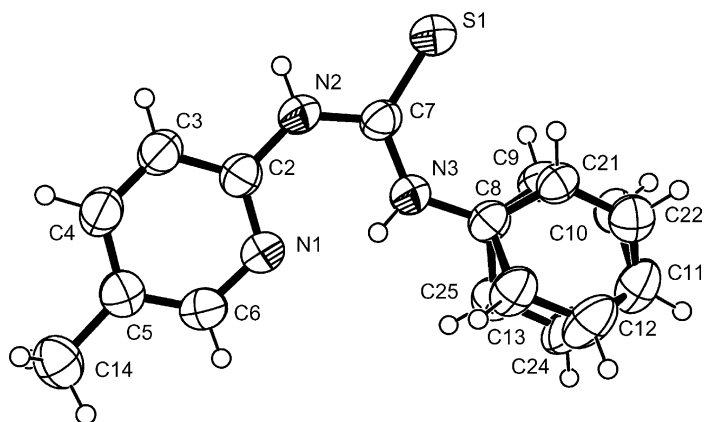


Fig. 4. Thermal ellipsoid plot of 5PicTuPh with atom numbering scheme and displacement ellipsoids at 50% probability level.

bonding interactions. The variation in the bond distances and angles in the crystallographically different molecules of 4PicTuPh is about the same as between the five thioureas.

Table 3 shows a comparison of the thiourea moiety bond distances and angles for the present thioureas with previously reported thioureas having an oxygen able to accommodate a hydrogen bond (i.e. BzOTup-NO₂Ph and BzOThpMeOPh) [6,7], *N*-(2-pyridyl)-*N'*-

phenylthiourea, PyTuPh [1], and *N,N'*-substituted thioureas that do not have intramolecular hydrogen bonding, PhTuPh and ChTuPh, *N,N'*-diphenylthiourea and *N*-cyclohexyl-*N'*-phenylthiourea, respectively [10,13]. The differences between the pyridyl thioureas and those with oxygen involved in the intramolecular hydrogen bond are: (1) N2–C7 bond is shorter (i.e. ca. three times the combined e.s.d.'s) and (2) S1–C7 bond is marginally longer

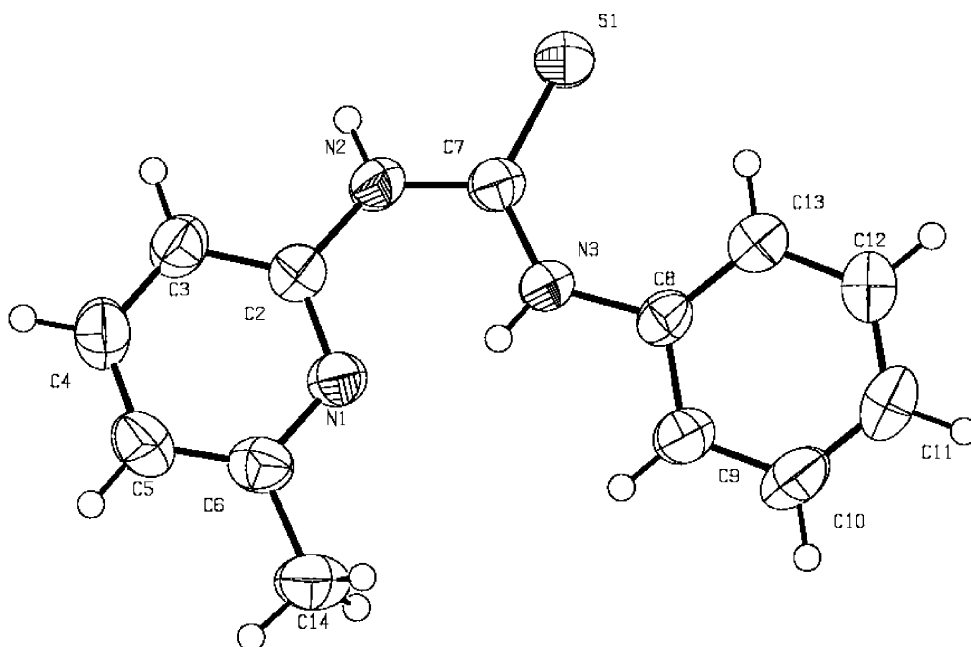


Fig. 5. Thermal ellipsoid plot showing 6PicTuPh with atom numbering scheme and displacement ellipsoids at 50% probability level.

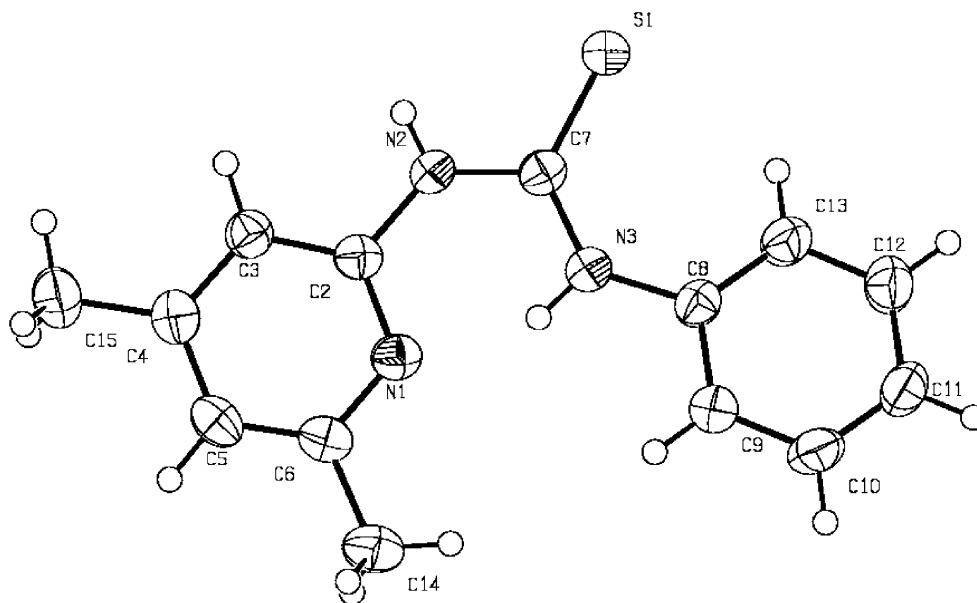


Fig. 6. Thermal ellipsoid plot showing 4,6LutTuPh with atom numbering scheme and displacement ellipsoids at 50% probability level.

(i.e. ca. two times their combined e.s.d.'s). There is essentially no difference in the N3–C7 bond as would be expected since both groups of thioureas have aromatic rings attached to N3. These 2-picolyl and

2-lutidyl thioureas do not have the electron withdrawing carbonyl group attached to N2, which allows the N2–C7 bond to have slightly more double bond character, but this bond is generally longer than found for thioureas without intramolecular hydrogen bonds [10,13]. There is no significant difference in the N2–C7–N3 bond angles between the two groups of intramolecularly hydrogen bonding thioureas, but both angles involving S1 show some difference. The N2–C7–S1 angle for the 2-picolyl and 2-lutidyl thioureas is smaller while the N3–C7–S1 angle is slightly larger compared to *N*-benzoyl thioureas [6,7]. *N*-cyclohexyl- and *N*-phenyl-*N'*-phenylthiourea (i.e. ChTuPh and PhTuPh, respectively) have a longer S1–C7 bond, and the present pyridyl thioureas, as well as *N*-pyridyl-*N'*-phenylthiourea, PyTuPh [1], have smaller N2–C7–S1 bond angles.

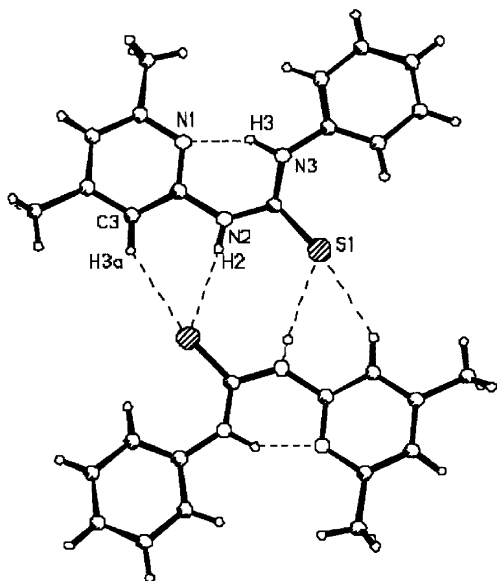


Fig. 7. Depiction of intramolecular and intermolecular hydrogen bonding in 4,6LutTuPh.

The N3–H3···N1 intramolecular interactions (Table 4) have similar N3···N1 distances indicating that position or extent of substitution on the pyridyl ring does not affect the strength of this interaction. However, the N–H···N angle does vary with the position of substitution in the order 3PicTuPh < 4PicTuPh < 5PicTuPh \cong 6 PicTuPh \cong 4,6LutTuPh. Like these thioureas, PyTuPh [1] has a N3–H···N(py) non-bonding distance of 2.646(4) Å. However, the angle for this N–H···N

Table 2
Selected bond distances (Å) and angles (°) for 3PicTuPh, 4PicTuPh, 5PicTuPh, 6PicTuPh and 4,6LutTuPh

	3PicTuPh	4PicTuPh ^a	5PicTuPh	6PicTuPh	4,6LutTuPh
<i>Bond</i>					
S1–C7	1.684(2)	1.676(3) 1.679(3)	1.672(3)	1.678(3)	1.687(3)
N1–C2	1.329(3)	1.320(4) 1.339(3)	1.324(3)	1.330(4)	1.335(4)
N1–C6	1.349(3)	1.348(5) 1.352(4)	1.349(4)	1.346(4)	1.346(4)
N2–C2	1.407(3)	1.411(4) 1.404(4)	1.405(3)	1.399(4)	1.408(4)
N2–C7	1.377(3)	1.367(4) 1.366(4)	1.369(3)	1.372(4)	1.367(4)
N3–C7	1.330(3)	1.330(4) 1.341(3)	1.340(3)	1.335(4)	1.339(4)
N3–C8	1.418(3)	1.420(4) 1.413(4)	1.416(3)	1.415(4)	1.418(4)
C2–C3	1.409(3)	1.397(4) 1.375(4)	1.389(4)	1.397(4)	1.387(4)
<i>Angle</i>					
C2–N1–C6	118.1(2)	115.8(4) 115.8(3)	116.7(3)	118.9(3)	118.4(2)
C2–N2–C7	131.3(2)	130.6(3) 131.0(3)	130.7(3)	130.8(2)	130.8(2)
C7–N3–C8	132.2(2)	133.1(4) 129.5(3)	130.2(3)	132.1(3)	132.6(3)
N1–C2–N2	117.8(1)	118.2(4) 117.5(3)	119.4(3)	118.8(2)	118.3(2)
N1–C2–C3	123.7(2)	123.9(3) 123.2(3)	122.2(3)	122.5(3)	122.9(3)
N2–C2–C3	118.5(2)	117.9(4) 119.3(4)	118.4(3)	118.6(3)	118.8(2)
S1–C7–N2	116.8(2)	118.1(3) 118.6(2)	118.5(2)	117.5(2)	117.7(2)
S1–C7–N3	127.8(2)	126.7(3) 125.7(3)	126.2(2)	126.7(2)	126.9(2)
N2–C7–N3	115.4(2)	115.1(3) 115.8(3)	115.3(3)	115.8(3)	115.4(2)
N3–C8–C9	114.9(2)	114.9(4) 116.2(3)	116.6(3) ^b	115.1(3)	114.9(3)
N3–C8–C13	125.4(2)	126.8(4) 123.6(3)	123.8(3) ^b	125.9(3)	126.1(3)

^a Second numbers refer to the second molecule of the two crystallographically unique molecules for 4PicTuPh, S1 and S2.

^b The N3–C8–C21 and N3–C8–C25 angles are 114.3(3) and 127.4(3), respectively, for the disordered phenyl ring.

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

Compound	Bond distances (Å)			Bond angles (°)			References
	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)	[10]
ChTuPh ^d	1.332(2)	1.696(2)	1.347(2)	117.3(2)	123.6(1)	119.1(1)	[13]
PyTuPh ^e	1.374(4)	1.682(3)	1.335(4)	116.8(5)	118.6(4)	124.6(4)	[1]
3PicTuPh	1.377(3)	1.684(2)	1.330(3)	115.4(2)	116.8(2)	127.8(2)	– ^f
4PicTuPh	1.367(4)	1.676(3)	1.330(4)	115.1(3)	118.1(3)	126.7(3)	– ^f
	1.366(4)	1.679(3)	1.341(3)	115.8(3)	118.6(2)	125.7(3)	– ^f
5PicTuPh	1.369(3)	1.672(3)	1.340(3)	115.3(3)	118.5(2)	126.2(2)	– ^f
6PicTuPh	1.372(4)	1.678(3)	1.335(4)	115.8(3)	117.5(2)	126.7(2)	– ^f
4,6LutTuPh	1.367(4)	1.687(3)	1.339(4)	115.4(2)	117.7(2)	126.9(2)	– ^f

^a *N*-benzoyl-*N'*-(4-nitrophenyl)thiourea.

^b *N*-benzoyl-*N'*-(4-methoxyphenyl)thiourea.

^c *N,N'*-diphenylthiourea.

^d *N*-cyclohexyl-*N'*-phenylthiourea.

^e *N*-(2-pyridyl)-*N'*-phenylthiourea.

^f This work.

Table 4

Intramolecular and intermolecular hydrogen bond distances (Å) and angles (°) for the various *N*-(2-pyridyl)-*N'*-(4-substituted phenyl)thioureas

<i>Intramolecular</i>						
Thiourea	D	A	D–H	H···A (Å)	D–H···A (Å)	∠(D–H···A) (°)
3PicTuPh	N3	N1	0.84(2)	1.92(2)	2.649(3)	145(2)
4PicTuPh	N3	N1	0.99(3)	1.75(4)	2.617(4)	144(3)
	N6	N4	0.93(3)	1.78(3)	2.627(4)	149(2)
5PicTuPh	N3	N1	0.83(3)	1.95(3)	2.648(4)	141(3)
6PicTuPh	N3	N1	0.83(4)	1.91(4)	2.647(3)	146(3)
4,6LutTuPh	N3	N1	0.87(3)	1.83(4)	2.633(4)	152(3)
<i>Intermolecular</i>						
3PicTuPh ^a	N2	S1#1	0.84(2)	3.15(3)	3.756(4)	145(2)
	C14	S1#1	0.96	2.95	3.896(3)	170.6
	C13	S1#2	0.96	2.98	3.766(4)	139.0
4PicTuPh ^b	N2	S1#1	1.01(4)	2.44(4)	3.413(3)	160(3)
	C3	S1#1	0.96(3)	2.93(3)	3.747(4)	143(2)
	N5	S2#2	0.80(3)	2.62(3)	3.397(3)	158(3)
	C23	S2#2	0.95(2)	3.01(2)	3.715(3)	132(2)
5PicTuPh ^{c,d}	N2	S2#1	0.86(3)	2.60(3)	3.440(3)	165(3)
	C3	S2#1	0.91(3)	2.85(3)	3.636(4)	144(3)
6PicTuPh ^e	N2	S1#1	0.87(4)	2.53(4)	3.387(3)	167(3)
	C3	S1#1	0.93	2.91	3.707(3)	144
4,6LutTuPh ^f	N2	S1#1	0.82(4)	2.66(4)	3.462(3)	165(3)
	C3	S1#1	0.93	2.88	3.660(3)	142

^a Symmetry transformations used to generate equivalent atoms: #1: 1 - x, -y, -z; #2: -1 + x, y, z.^b Symmetry transformations used to generate equivalent atoms: #1: 1 - x, -y, -z; #2: 1 - x, -y, 1 - z.^c Angle between the mean planes of the pyridine rings: S1/S2 = 59.64(0.12)°.^d #1: -x, 2 - y, 1 - z.^e #1: 2 - x, -y, 1 - z.^f #1: -x, 1 - y, -z.

interaction is 132.8(2.1)°, which is smaller than found for any compounds in this study.

As was found for *N*-benzoyl-*N'*-(4-methoxyphenyl)thiourea [7], NH is involved in intermolecular hydrogen bonding with a sulfur from a neighboring molecule. Using the non-bonding N···S distance as a measure of the strength of this interaction, the order of strength is as follows: 6PicTuPh > 4PicTuPh (both molecules) > 5PicTuPh > 4,6LutTuPh ≫ 3PicTuPh. The comparatively long distance found for 3PicTuPh is indicative of the steric effect of the methyl group in this position. The next longest is 4,6-LutTuPh, and the two methyl groups may also exert a steric effect; the weaker dimer formation is probably due to packing of the layers of dimers since greater volume is required by the additional methyl group. The non-bonding N···S distance is 3.592(2) Å for *N*-benzoyl-*N'*-(4-methoxyphenyl)thiourea, while other *N*-substituted and *N,N'*-substituted thioureas average 3.46 Å [10–14], the smallest distance being 3.363(1) Å for *N*-

diethyl-*N'*-*o*-tolylthiourea [12] and the largest 3.563(1) Å for *N*-cyclohexyl-*N'*-cyclohexylthiourea [11]. The present compounds have an average N···S distance of 3.488(7) Å, which is within the above range. The intermolecular N–H···S bond angle for 3PicTuPh, an average of 145(2)°, is much smaller than the other thioureas of this study, which average more than 160°. This latter angle falls in the range between 140(3)° (*N*-dimethyl-*N'*-*o*-tolylthiourea) [12] and 170(1)° (*N*-ethyl-*N'*-ethylthiourea) [14]. Therefore, 3PicTuPh has the weakest intermolecular N–H···S interaction among *N*-(2-pyridyl)thioureas [1,16–20] reported to date, which is consistent with it having the lowest melting point, 122–124 °C. Fig. 7 shows that C3H of 4,6LutTuPh, absent in 3PicTuPh, is positioned to interact with a neighboring molecule's S1 in conjunction with N2H when the pyridyl ring and thiourea moiety are approximately coplanar. The distances and angles for this interaction is included in Table 4. The thiourea with molecules having

Table 5
Mean plane data and angles between planes for 3PicTuPh, 4PicTuPh, 5PicTuPh, 6PicTuPh and 4,6LutTuPh

Compound	Plane #	Plane	Mean plane deviation	Atom with greatest deviation	Plane/plane	Angle
3PicTuPh	1	N1–C2–C3–C4–C5–C6	0.0026	C3, 0.0043(0.0015)	1/2	8.05(0.10)
	2	N2–C7–S1–N3	0.0039	C7, 0.0068(0.0017)	2/3	15.69(0.11)
	3	C8–C9–C10–C11–C12–C13	0.0040	C8, 0.0057(0.0016)	1/3	9.07(0.12)
4PicTuPh	1	N1–C2–C3–C4–C5–C6	0.0003	C3, 0.0053(0.0030)	1/2	3.46(0.14)
	2	N2–C7–S1–N3	0.0001	C7, 0.0011(0.0030)	2/3	8.77(0.30)
	3	C8–C9–C10–C11–C12–C13	0.0001	C8, 0.0031(0.0030)	1/3	5.95(0.24)
	4	N4–C22–C23–C24–C25–C26	0.0004	C23, 0.0062(0.0032)	4/5	6.95(0.28)
	5	N5–C27–S2–N6	0.0004	C7, 0.0033(0.0031)	5/6	43.55(1.46)
	6	C28–C29–C30–C31–C32–C33	0.0007	C9, 0.0125(0.0039)	4/6	42.45(1.76)
5PicTuPh	1	N1–C2–C3–C4–C5–C6	0.0084	C5, 0.0127(0.0020)	1/2	4.55(0.14)
	2	N2–C7–S1–N3	0.0002	C7, 0.0003(0.0021)	2/3	33.26(0.21)
	3	C8–C9–C10–C11–C12–C13	0.0401	C11, 0.0655(0.0046)	1/3	34.89(0.20)
	4	C8–C21–C22–C11–C24–C25	0.0079	C21, 0.0123(0.0040)	3/4	59.84(0.22)
6PicTuPh	1	N1–C2–C3–C4–C5–C6	0.0034	C5, 0.0048(0.0023)	1/2	3.96(0.21)
	2	N2–C7–S1–N3	0.0002	C7, 0.0003(0.0024)	2/3	11.11(0.10)
	3	C8–C9–C10–C11–C12–C13	0.0019	C9, 0.0030(0.0023)	1/3	11.07(0.21)
4,6LutTuPh	1	N1–C2–C3–C4–C5–C6	0.0037	C3, 0.0056(0.0019)	1/2	4.65(0.17)
	2	N2–C7–S1–N3	0.0000	C7, 0.0001(0.0022)	2/3	13.13(0.17)
	3	C8–C9–C10–C11–C12–C13	0.0052	C8, 0.0084(0.0021)	1/3	13.91(0.17)

crystallographic differences, 4PicTuPh, could intermolecularly hydrogen bond between either crystallographically identical or different molecules; 4PicTuPh forms hydrogen bonds between crystallographically identical molecules.

The angles between planes often provide information about the molecules' geometry with the angle between the pyridyl and aryl mean planes being a convenient measure for the present compounds, Table 5. This angle is very different between the two crystallographic unique molecules of 4PicTuPh, 5.95(0.24) and 42.45(1.76)°. The other thioureas of this study, except for 5PicTuPh, have an angle ranging from 9 to 14° between the pyridine and aryl mean planes. It should be noted that substitution on the

aryl ring causes this angle to be much larger; the angle between the pyridine ring and aryl ring for *N*-(2-pyridyl)-*N'*-2-tolyl-, *N*-(2-pyridyl)-*N'*-3-tolyl- and *N*-(2-pyridyl)-*N'*-4-tolylthiourea is 67.4(1)°, averages 79.4(1)° (two unique molecules) and 58.7(1)° (two unique molecules), respectively [16]. The angle between the mean planes of the pyridine ring and thiourea moiety is larger for 3PicTuPh, ca. 8°, than the other thioureas of this study, ca. 4°. The larger angle for 3PicTuPh results in greater distance between the 3-methyl group hydrogens and the hydrogen attached to N2 and results in weaker intermolecular N2–H···S1 hydrogen bonding as discussed earlier.

3.2. Thermal studies

The DSC plots of these thioureas show a sharp peak due to melting followed immediately by a broader peak representing decomposition. Representative enthalpies of fusion are as follows: PyTuPh, 41.0; 6PicTuPh, 43.5 and 4,6LutTuPh, 50.9 kJ mol⁻¹. The TGA experiments show loss of 100% of their mass at temperatures beginning within 10° of their melting points and ending approximately 20° above their melting points with no mass loss preceding this one step process.

Table 6
¹H NMR and ultraviolet spectral data for PhTu, 3PicTuPh, 4PicTuPh, 5PicTuPh, 6PicTuPh and 4,6LutTuPh

Compound	<i>N'</i> H	NH	n → π*
PhTu	13.865	10.903	32 900(4.429) ^a
3PicTuPh	13.930	8.268	32 680(4.350)
4PicTuPh	13.739	9.027	33 220(4.462)
5PicTuPh	13.648	9.559	32 680(4.317)
6PicTuPh	14.103	9.205	32 470(4.468)
4,6LutTuPh	14.119	8.311	32 680(4.443)

^a log ε.

3.3. Spectral studies

The UV spectra (CHCl_3) show two strong bands which we assign to a combination of $\pi \rightarrow \pi^*$ transitions from both rings and an $n \rightarrow \pi^*$ (Table 6) of the heterocyclic ring. The former band appears at $37\,000\text{ cm}^{-1}$ in these thioureas and is somewhat weaker than the latter band, which has a molar absorptivity of ca. 2.8×10^4 . Based on the spectra of thiosemicarbazones, which show a band associated with the thioamide part of the molecule in the $25\,000\text{ cm}^{-1}$ region, $n \rightarrow \pi^*$ transitions involving sulfur non-bonding electrons are observed as shoulders in the spectra of some of these thioureas at ca. $28\,000\text{ cm}^{-1}$. In the infrared spectra of these thioureas ($\nu(\text{NH})$ is an absorption of medium intensity at ca. 3200 cm^{-1} and $\nu(\text{CS})$ appears between 820 and 860 cm^{-1} region.

The ^1H NMR spectra, including the spectrum of PyTuPh, Table 6, show considerable variation in the position of the resonance of the intramolecular hydrogen bonding N3H. The presence of methyl groups in the 6-position on the pyridyl ring (i.e. 6PicTuPh and 4,6LutTuPh) provides shielding to the N3H resonance due to the diamagnetic anisotropic effect of the C6–CH₃ bond. An upfield shift of larger magnitude occurs for the resonance assigned to N2H with additional methyl groups on the pyridyl ring. There is no difference in the ^{13}C resonance of the thione carbon, ca. 178 ppm, with change in the number of methyl groups on the pyridyl ring.

4. 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-154847 for 3PicTuPh, CCDC-156363 for 4PicTuPh, CCDC-156364 for 5PicTuPh, CCDC-156770 for 6PicTuPh and CCDC-156771 for 4,6LutTuPh. 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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