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Structural, spectral and thermal studies of *N*-2-(pyridyl)- and *N*-2-(picolyl)-*N*′-(3-chlorophenyl)thioureas

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Abstract

N-2-(pyridyl)-*N*′-3-chlorophenylthiourea, PyTu3Cl, monoclinic, $P2_1$, $a = 9.9770(14)$, $b = 6.1770(9)$, $c = 9.9000(7)$ Å, $\beta = 97.301(8)°$, $V = 605.17(13)$ Å^3 and $Z = 2$; *N*-2-(4-picolyl)-*N*′-3-chlorophenylthiourea, 4PicTu3Cl, triclinic, $P-1$, $a = 4.7970(3)$, $b = 10.7180(12)$, $c = 12.7370(15)$ Å, $\alpha = 77.919(4)$, $\beta = 85.959(6)$, $\gamma = 89.697(7)°$, $V = 638.74(11)$ Å^3 and $Z = 2$; *N*-2-(5-picolyl)-*N*′-3-chlorophenylthiourea, 5PicTu3Cl, monoclinic, $P2_1/c$, $a = 11.1580(6)$, $b = 15.233(2)$, $c = 7.5118(15)$ Å, $\beta = 93.336(8)°$, $V = 1274.5(3)$ Å^3 and $Z = 4$ and *N*-2-(6-picolyl)-*N*′-3-chlorophenylthiourea, 6PicTu3Cl, triclinic, $P-1$, $a = 7.3620(12)$, $b = 8.828(3)$, $c = 11.675(3)$ Å, $\alpha = 98.78(1)$, $\beta = 104.398(17)$, $\gamma = 109.651(16)°$, $V = 668.5(2)$ Å^3 and $Z = 2$. The intramolecular hydrogen bonding between N′H and the pyridine nitrogen and intermolecular hydrogen bonding involving the thione sulfur and the NH hydrogen, as well as the planarity of the molecules, are affected by the presence and position of the methyl substituent on the pyridine ring. ^{1}H NMR studies in $CDCl_3$ show the NH′ hydrogen resonance considerably downfield from other resonances in their spectra indicating intramolecular hydrogen bonding is also present in solution.

Keywords: 2-Pyridylthioureas; Chlorophenylthioureas; Crystal structures; Hydrogen bonding; Enthalpy of fusion

1. Introduction

Numerous structural studies of *N*-2-pyridyl-*N*′-arylthioureas with substituents on either or both rings have recently appeared [1–8]. Although there are not large differences in bond distances and angles among these thioureas, other structural parameters have shown substantial variation. Intramolecular N′–H···N and intermolecular N–H···S hydrogen bonding, as well as the planarity of the molecules, are representative of these structural parameters that are affected by substitution on either or both rings. Previously, the *N*-2-(4,6-lutidyl)-*N*′-chlorophenylthioureas [9] were the subject of one study and this was followed by a studies of the *N*-2-picolyl-*N*′-4-chlorophenylthioureas [10] and *N*-2-picolyl-*N*′-2-chlorophenylthioureas [11]. Involvement of the chloro substituent in various interactions with hydrogens was described, and we report here a similar study

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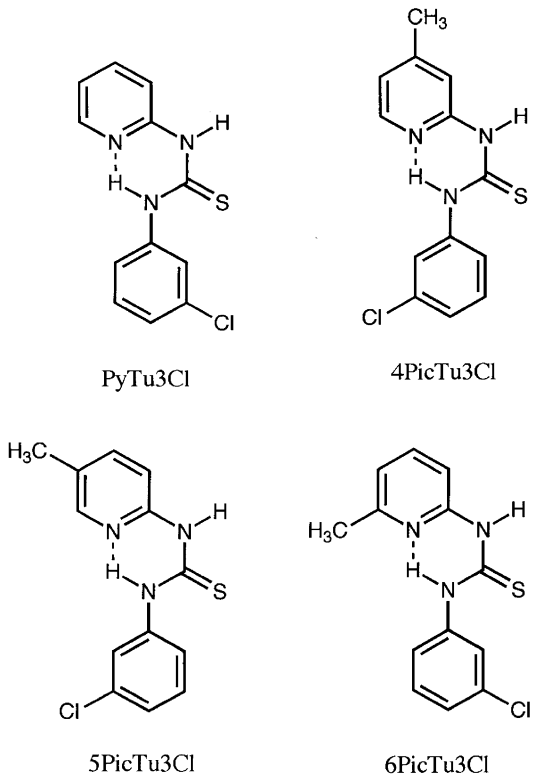

Fig. 1. Depiction of *N*-2-pyridyl-*N*′-3-chlorophenylthiourea, PyTu3Cl; *N*-2-(5-picolyl)-*N*′-3-chlorophenylthiourea, 5PicTu2Cl and *N*-2-(6-picolyl)-*N*′-3-chlorophenylthiourea, 6PicTu3Cl.

of the *N*-2-picolyl-*N*′-3-chlorophenylthioureas and *N*-2-pyridyl-*N*′-3-chlorophenylthiourea, Fig. 1.

2. Experimental

2-Aminopyridine, the 2-aminopicolines and 3-chlorophenyl isothiocyanate were purchased from Aldrich and used as received. 2-Aminopyridine or a 2-aminopicoline was mixed in a 1:1 molar ratio with 3-chlorophenyl isothiocyanate 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 and dried on a warm plate. The yields are ca. 75% for each of the thioureas and their melting points are listed in Table 5 with the ΔH's of fusion. The ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker 200 MHz spectrometer and the enthalpies of fusion were obtained with approximately 3 mg samples at a heating rate of 10 °C/min using a Perkin–Elmer Differential Scanning Calorimeter, DSC7.

Crystals of the thioureas were grown by slow evaporation of 1:1 by volume acetone–anhydrous ethanol mixtures at room temperature. The colorless thiourea crystals were mounted in random orientation on a glass fiber on a Nonius Kappa CCD Diffractometer, Mo Kα ($\lambda = 0.71073$ Å). Cell constants and an orientation matrix for data collections were obtained by least squares refinements of the diffraction data from more than 500 reflections. The structures were solved by direct methods and missing atoms were found by difference-Fourier synthesis. The non-hydrogen atoms were refined with anisotropic temperature factors, and all hydrogens attached to nitrogens and carbons, except for methyl groups and the CH's of 4PicTu3Cl which were fixed and refined using a riding model, were found on a difference-Fourier map and refined isotropically. Scattering factors are from Waasmaier and Kirfel [12]. The structures were solved with MaXus [13], structure refinement was carried out with SHELXL-97 [14] and the graphics used are ZORTEP [15]. Table 1 summarizes the crystal data, collection information and refinement data for these thioureas.

3. Results and discussion

3.1. Structural studies

Suitable crystals were obtained for *N*-2-(pyridyl)-*N*′-(3-chlorophenyl)thiourea, PyTu3Cl; *N*-2-(4-picolyl)-*N*′-(3-chlorophenyl)thiourea, 4PicTu3Cl; *N*-2-(5-picolyl)-*N*′-(3-chlorophenyl)thiourea, 5PicTu3Cl and *N*-2-(6-picolyl)-*N*′-(3-chlorophenyl)thiourea, 6PicTu3Cl. Although a number of solvents and solvent mixtures were tried, we were unable to obtain suitable crystals of *N*-2-(3-picolyl)-*N*′-(3-chlorophenyl)thiourea, 3PicTu3Cl; the structure of *N*-2-(4,6-lutidyl)-*N*′-(3-chlorophenyl)thiourea, 4,6LutTu3Cl, was included in an earlier publication [9]. Selected bond distances and angles are listed in Table 2, the hydrogen bonding parameters are listed in Table 3 and

Table 1
Crystallographic data and methods of data collection, solution and refinement for PyTu3Cl, 4PicTu3Cl, 5PicTu3Cl and 6PicTu3Cl

Crystal data	PyTu3Cl	4PicTu3Cl	5PicTu3Cl	6PicTu3Cl
Empirical formula	$C_{12}H_{10}ClN_3S$	$C_{13}H_{12}ClN_3S$	$C_{13}H_{12}ClN_3S$	$C_{13}H_{12}ClN_3S$
Type of radiation and its wavelength (Å)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Type of diffractometer used for data collection	Nonius Kappa-CCD Diffract.	Nonius Kappa-CCD Diffract.	Nonius Kappa-CCD Diffract.	Nonius Kappa-CCD Diffract.
Temperature	293(2)	130(2)	130(2)	293(2)
Crystal color, habit	Colorless, prism	Colorless, needle	Colorless, plate	Colorless, prism
Crystal size (mm)	$0.12 \times 0.12 \times 0.05$	$0.96 \times 0.12 \times 0.12$	$0.67 \times 0.26 \times 0.02$	$0.12 \times 0.12 \times 0.05$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1$ (#4)	$P-1$ (#2)	$P2_1/c$ (#14)	$P-1$ (#2)
a (Å)	9.9770(14)	4.7970(3)	11.1580(6)	7.3620(12)
b (Å)	6.1770(9)	10.7180(12)	15.233(2)	8.828(3)
c (Å)	9.9000(7)	12.7370(12)	7.5118(15)	11.675(3)
α (°)	90	77.919(4)	90	98.78(1)
β (°)	97.301(8)	85.959(6)	93.336(8)	104.398(17)
γ (°)	90	89.697(7)	90	109.651(16)
Volume (Å^3)	605.17(13)	638.74(11)	1274.5(3)	668.5(2)
Z	2	2	4	2
Formula weight	263.74	277.77	277.77	277.77
Density (calcd) (g/cm$^{3)}$	1.447	1.444	1.448	1.380
Absorp. coeff. (mm^{-1})	0.467	0.446	0.447	0.427
F(000)	272	288	576	288
Index ranges	$-12 \le h \le 12$; $-6 \le k \le 7$; $-10 \le l \le 10$	$-5 \le h \le 5$; $-13 \le k \le 10$; $-14 \le l \le 15$	$0 \le h \le 12$; $-16 \le k \le 16$; $-8 \le l \le 8$	$-8 \le h \le 7$; $-9 \le k \le 10$; $-11 \le l \le 13$
θ range for data collection	3.89–26.35	3.28–26.35	3.24–23.25	3.06–24.71
Total reflections/parameters	1873/194	2310/200	3122/200	3150/200
Independent reflects., R_{int}	1481, 0.046	1616, 0.0299	1795, 0.0467	2088, 0.0628
Absorption correction	HKL-Scalepack	HKL-Scalepack	HKL-Scalepack	HKL-Scalepack
Max., min. transmissions	0.9770, 0.9461	0.9484, 0.6739	0.9911, 0.7536	0.9790, 0.9506
Goodness-of-fit	1.054	1.055	0.948	0.765
Largest diff. peak (eÅ^{-3})	0.269	0.188	0.233	0.193
Largest diff. hole (eÅ^{-3})	−0.270	−0.260	−0.221	−0.196
R_1, wR_2	0.0478, 0.0872	0.0393, 0.0893	0.0379, 0.0734	0.0507, 0.0975
R_1, wR_2 (all reflections)	0.0810, 0.0940	0.0696, 0.0980	0.0729, 0.0820	0.1827, 0.1319

the mean plane data in Table 4. ORTEP drawings for PyTu2Cl, 4PicTu3Cl, 5PicTu3Cl and 6PicTu3Cl are shown in Figs. 2–5, respectively. Fig. 6 shows the intermolecular hydrogen bonding of 5PicTu3Cl to form the dimer characteristic of *N*-2-pyridyl-*N*′-arylthioureas [1–11].

Like other 2-pyridylthioureas [1–11], PyTu3Cl, 4PicTu3Cl, 5PicTu3Cl and 6PicTu3Cl are found in a conformation resulting from intramolecular hydrogen bonding of N3H (N′H) to the pyridine nitrogen, N1, Figs. 1–4. If these thioureas are visualized in two dimensions the chloro substituent is on the sulfur side of the thiourea moiety in PyTu3Cl and 6PicTu3Cl, as was found for 4,6LutTu3Cl [9], but opposite to the sulfur in 4PicTu4Cl, and 5PicTu3Cl. Although there is some variation in the bond distances, Table 2, the variations lack a trend and are within twice the combined esd values. In contrast, the bond angles show some variation; the angles of 4PicTu3Cl and 6PicTu3Cl are substantially different. The angles with the largest difference, which are similar to the analogous angles in 4,6LutTu3Cl [9], are not close to the pyridine ring suggesting that the difference is due to a packing effect caused by the position of methyl substituent(s) on the pyridine ring.

Table 2
Selected bond distances (Å) and angles (°) for PyTu3Cl, 4PicTu3Cl, 5PicTu3Cl and 6PicTu3Cl

Distances (Å)	PyTu3Cl	4PicTu3Cl	5PicTu3Cl	6PicTu3Cl
S1–C7	1.690(4)	1.686(2)	1.683(3)	1.674(5)
N1–C2	1.329(5)	1.328(3)	1.333(4)	1.322(6)
N1–C6	1.353(5)	1.346(3)	1.346(4)	1.346(6)
C2–N2	1.397(5)	1.397(3)	1.400(4)	1.391(6)
N2–C7	1.364(5)	1.370(3)	1.368(4)	1.380(6)
N3–C7	1.332(5)	1.334((3)	1.340(4)	1.339(6)
N3–C8	1.433(5)	1.424(3)	1.430(4)	1.410(6)
C10–Cl1	1.746(4)	1.745(2)	1.749(3)	1.734(5)
Angles (°)				
C2–N1–C6	116.6(4)	116.96(17)	117.1(3)	119.5(5)
N1–C2–C3	123.5(4)	123.13(19)	122.8(3)	122.6(5)
N1–C2–N2	118.8(4)	118.65(18)	118.6(3)	118.6(5)
N2–C2–C3	117.6(4)	118.2(2)	118.5(3)	118.7(5)
C2–N2–C7	130.4(4)	130.4(2)	131.0(3)	130.3(5)
S1–C7–N2	118.8(3)	118.19(17)	119.0(2)	117.8(4)
N2–C7–N3	117.3(4)	116.30(19)	117.7(3)	114.8(5)
S1–C7–N3	123.9(3)	125.50(16)	123.3(2)	127.4(4)
C7–N3–C8	123.1(3)	127.5(2)	124.2(3)	131.8(5)

An intermolecular N2H2···S1 interaction is generally present in substituted thioureas, Fig. 6, with intramolecular hydrogen bonding to an oxygen [16–23] or nitrogen atom [1–11], as well as thioureas without intramolecular hydrogen bonding [24–28]. The N2···S1 non-bonding distance for 5PicTu3Cl is substantially shorter than for the other thioureas of this study, as well as 4,6LutTu3Cl, 3.466(4) Å [9], and there are also differences for the H2···S1 distance and N2–H2···S1 angle. In a similar comparison with the analogous 2-chloro derivatives 4,6LutTu2Cl had the shortest N2···S1 non-bonding distance, which was suggested to be due to a small additional electronic effect of the second methyl group on the pyridine ring [11]. However, the aryl ring is positioned so that the chloro substituents in that series are located opposite to the thiourea sulfur. Therefore, the stronger hydrogen bonding interaction (i.e. based on shorter N2···S1 and H2···S1 distances) in 5PicTu3Cl (and 4PicTu3Cl) probably results from a lack of a steric effect of the chloro substituent that is presumably present in

Table 3
Intramolecular and intermolecular hydrogen bond distances (Å) and angles (°) for PyTu3Cl, 4PicTu3Cl, 5PicTu3Cl and 6PicTu3Cl

Thiourea	D	A	D–H	H···A	D–H···A	∠(D–H···A)
Intramolecular						
PyTu3Cl	N3	N1	0.94(5)	1.91(4)	2.664(4)	135(4)
4PicTu3Cl	N3	N1	0.88(2)	1.91(2)	2.649(2)	141(2)
5PicTu3Cl	N3	N1	0.92(3)	1.92(3)	2.688(3)	141(3)
6PicTu3Cl	N3	N1	1.14(6)	1.64(6)	2.610(6)	139(5)
Intermolecular						
PyTu3Cl[a]	N2	S1#1	0.83(4)	2.62(5)	3.415(4)	161(4)
	C3	S2#1	0.97(4)	2.91(4)	3.748(5)	145(3)
	C11	N1#2	1.02(4)	2.88(4)	3.602(5)	128(3)
	N3	Cl1#2	0.94(5)	2.92(5)	3.613(4)	132(4)
	C13	S1#3	0.92(4)	2.87(5)	3.618(5)	139(3)
4PicTu3Cl[b]	N2	S1#1	0.85(2)	2.58(2)	3.373(2)	155(2)
	C3	S1#1	0.91(2)	2.93(2)	3.631(2)	134.5(14)
	C6	Cl1#2	0.90(2)	2.97(2)	3.694(2)	137.7(15)
	C9	N1#2	0.89(2)	2.87(2)	3.310(3)	112.0(16)
5PicTu3Cl[c]	N2	S1#1	0.81(3)	2.51(3)	3.315(3)	169(3)
	C3	S1#1	0.93(3)	2.84(3)	3.620(3)	142(2)
	C6	N1#2	0.90(3)	2.95(3)	3.763(4)	152(2)
	C9	S1#2	0.99(3)	2.81(3)	3.705(3)	151(2)
	C13	Cl1#3	0.95(3)	2.94(3)	3.673(3)	136(2)
6PicTu3Cl[d]	N2	S1#1	0.82(5)	2.66(5)	3.424(6)	155(5)
	C3	S1#1	1.02(5)	2.73(5)	3.636(7)	148(3)

[a] #1: $-x$, $0.5+y$, $1-z$; #2: $-x$, $-0.5+y$, $-z$; #3: x, $-1+y$, z.
[b] #1: $1-x$, $1-y$, $1-z$; #2: $-x$, $-y$, $2-z$; #3: $-1+x$, y, z.
[c] #1: $2-x$, $-y$, $-z$; #2: x, $0.5-y$, $0.5+z$; #3: $3-x$, $-0.5+y$, $0.5-z$.
[d] #1: $1-x$, $-y$, $2-z$.

Table 4
Mean plane data and angles between planes for PyTu3Cl, 4PicTu3Cl, 5PicTu3Cl and 6PicTu3Cl

Compound	Plane	Plane #	Mean plane deviation	Atom with greatest deviation	Plane/plane	Angle
PyTu3Cl	N1–C2–C3–C4–C5–C6	1	0.0040	C3, 0.0067(0.0031)	2/1	6.65(0.27)
	N2–C7–S1–N3	2	0.0030	C7, 0.0052(0.0031)	3/2	86.40(0.12)
	C8–C9–C10–C11–C12–C13	3	0.0021	C11, 0.0035(0.0028)	1/3	80.44(0.12)
4PicTu3Cl	N1–C2–C3–C4–C5–C6	1	0.0061	C4, 0.0089(0.0015)	2/1	8.71(0.14)
	N2–C7–S1–N3	2	0.0025	C7, 0.0044(0.0017)	3/2	45.20(0.08)
	C8–C9–C10–C11–C12–C13	3	0.0086	C8, 0.0130(0.0016)	1/3	39.56(0.08)
5PicTu3Cl	N1–C2–C3–C4–C5–C6	1	0.0011	C5, 0.0017(0.0022)	2/1	1.51(0.18)
	N2–C7–S1–N3	2	0.0006	C7, 0.0010(0.0024)	3/2	58.21(0.09)
	C8–C9–C10–C11–C12–C13	3	0.0068	C11, 0.0074(0.0020)	1/3	56.77(0.10)
6PicTu3Cl	N1–C2–C3–C4–C5–C6	1	0.0025	C3, 0.0043(0.0038)	2/1	7.80(0.28)
	N2–C7–S1–N3	2	0.0040	C7, 0.0070(0.0042)	3/2	14.37(0.19)
	C8–C9–C10–C11–C12–C13	3	0.0050	C9, 0.0085(0.0037)	1/3	6.59(0.18)

PyTu3Cl, 6PicTu3Cl and 4,6LutTu3Cl. In addition, the sulfur in the neighboring molecule is located between N2 and C3 of the pyridine ring so that it also interacts with C3H3 in these thioureas, Fig. 6. The sulfur–hydrogen distances for the C3H3···S1 interactions are not much longer (i.e. 0.15–0.30 Å) compared to the H2···S1 distances for the N2H2···S1 interactions. Other C–H···X interactions in which a hydrogen is less than 3.00 Å from X, and the angle is larger than 110° are listed in Table 3. In PyTu3Cl there is a weak interaction between N3H3 and a Cl atom of another neighboring molecule, while one of the *ortho* hydrogens of the phenyl ring interacts with a neighboring Cl. Similar interactions are present in the crystals of 4PicTu3Cl and 5PicTu3Cl, but the H···X distances in 6PicTu3Cl are >3.0 Å.

The non-bonding N3···N1 distances for the intramolecular hydrogen bonding interaction of these thioureas differ significantly, but the angles for the N3–H3···N1 interaction are within the range 135 and 150°, that has been found for previously studied thioureas attached to a pyridine ring [1–11]. Similarly, 4,6LutTu3Cl has a N3···N1 distance of 2.643(4) Å and ∠N3H3···N1 is 147(3)°. Therefore, 6PicTu3Cl, which has the weakest intermolecular N2H2···S1 interaction, has the strongest N3H3···N1 interaction based on H3···N1 and N3···N1 distances.

The data for the mean planes are shown in Table 4, and there is a large difference in the planarity of the four molecules. The angle between the mean planes of the pyridyl and aryl ring, as a measure of planarity, is a useful parameter. This is particularly true since the angle between the mean planes of the pyridine ring and the thiourea moiety do not show large variation; they are less than 15° for the *N*-2-pyridyl-*N*′-arylthioureas studied to date [1–11] and the thioureas of this study are in this range. The angle between the mean planes of the two rings in

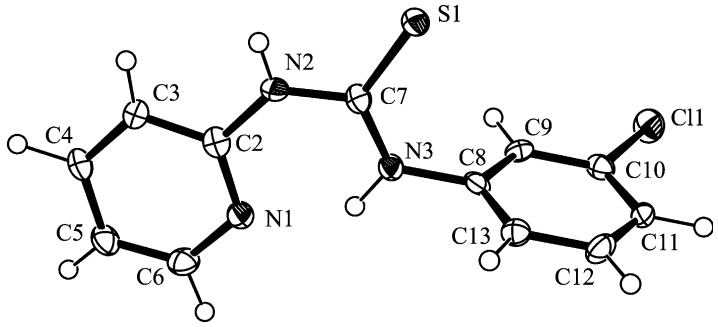

Fig. 2. ORTEP diagram showing PyTu3Cl with atom numbering scheme and displacement ellipsoids at 50% probability level.

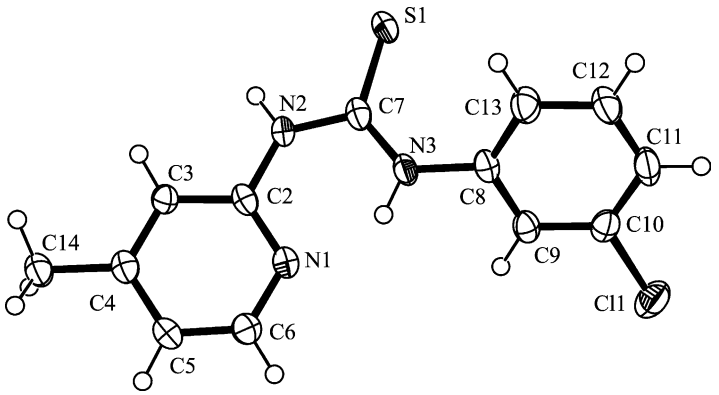

Fig. 3. ORTEP diagram showing 4PicTu3Cl with atom numbering scheme and displacement ellipsoids at 50% probability level.

the order PyTu3Cl > 5PicTu3Cl > 4PicTu3Cl > 6 PicTu3Cl > 4,6LutTu3Cl, 3.01(0.15)° [9].

In order to compare the effect of different substituents in the 3-position of the aryl ring, we have compiled Table 5 (a listing of angles between the mean planes of the rings and intramolecular and intermolecular hydrogen bonding parameters) for a number of *N*-2-pyridylthioureas with solved crystal structures. A similar comparison of *N*-2-pyridylthioureas with substituents in the 2-position of the aryl ring [29] allowed identification of some interesting relationships in that series. For example, a decreasing angle between rings causes shorter non-bonding distances, *d*(N3···N1), for the *N*-2-(4-picolyl)-*N′*-arylthioureas and an increase in *d*(N2···S1) for the *N*-2-(5-picolyl)-*N′*-arylthioureas [29]. For the *N*-2-pyridyl-*N′*-(3-substituted)arylthioureas listed first in Table 5, there is not a correlation for the angle between the mean planes of the two rings and any of the hydrogen bonding parameters. In contrast, like the their 2-substituted analogues [29], the *d*(N3···N1) distance decreases, as does the *d*(N2···S1) distance, with decrease in the angle between planes for the 4PicTu's. The 5PicTu's may show a trend in the intermolecular N2H2···S1 angle, but the structure of at least one more thiourea is needed to confirm this trend. The 6PicTu's and 4,6LutTu's in Table 5, in contrast to their 2-substituted analogues [29], do not show any trend other than a similarity in angle between planes and the nature of the 3-aryl substituent.

3.2. Thermal studies

The DSC plots of these thioureas show a sharp peak due to melting, and values for ΔH_{fus} are shown in

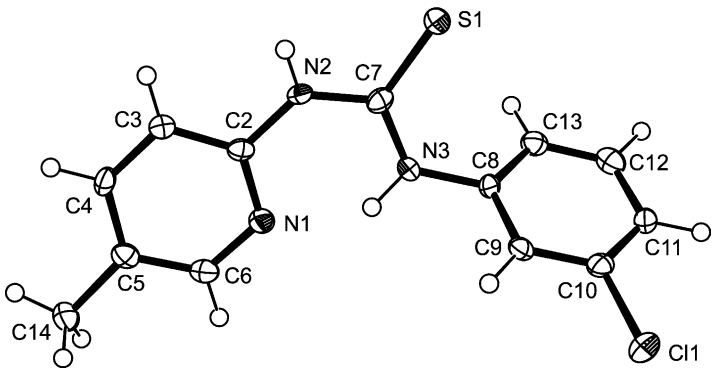

Fig. 4. ORTEP diagram showing 5PicTu3Cl with atom numbering scheme and displacement ellipsoids at 50% probability level.

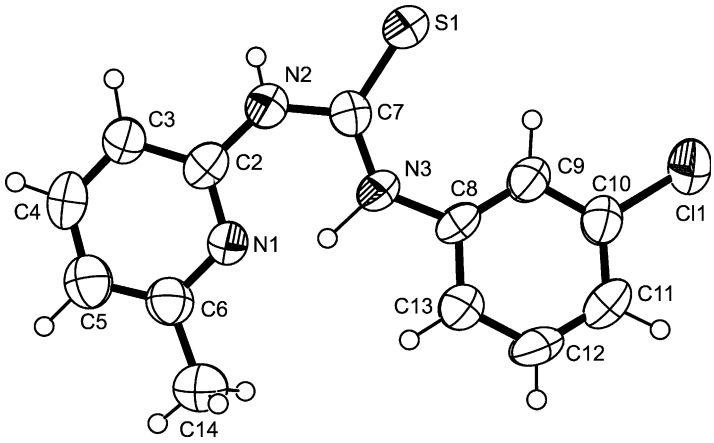

Fig. 5. ORTEP diagram showing 6PicTu3Cl with atom numbering scheme and displacement ellipsoids at 50% probability level.

Table 6 along with their melting points. Values for *N*-(2-pyridyl)-*N*-2-(4,6-lutidyl)-*N′*-3-chlorophenylthiourea [9] are included. Although, several intermolecular interactions are listed in Table 3, these interactions do not seem to affect the ΔH_{fus} values, which are not very different. The low melting point for 3PicTu3Cl, which has been observed for 3PicTu's of other series, results from the 3-methyl group reducing the strength of the N–H···S interaction.

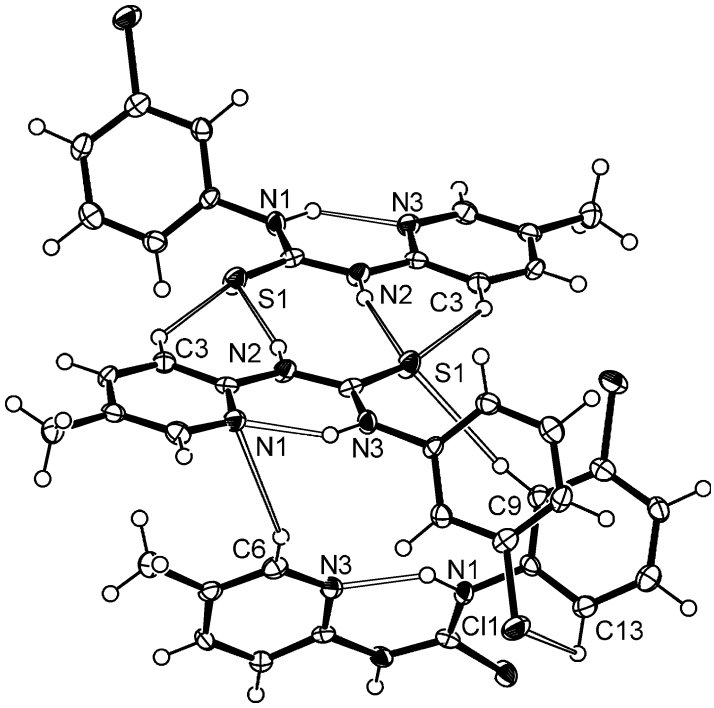

Fig. 6. Partial packing diagram for 5PicTu3Cl showing the intramolecular N3–H3···N1 and intermolecular interactions (open lines).

Table 5
A comparison of hydrogen bonding distances and angles with the angle between the mean planes of the pyridyl and aryl rings for various series of *N*(2)-pyridyl-*N′*-(3-subsituted) arylthioureas

Thiourea	∠pyridyl/aryl	*d*(N3···N1)	∠(N3–H···N1)	*d*(N2···S1)	∠(N2–H···S1)	Reference
PyTu3OMe	89.7(1)	2.657(4)	132(4)	3.410(4)	153(3)	[30]
PyTu3Cl	80.4(1)	2.664(4)	135(4)	3.415(4)	161(4)	This work
PyTu3T	79.4(1)	2.698(3)	132(2)	3.393(3)	156(2)	[31]
PyTuPh	63.2(1)	2.646(4)	133(2)	3.412(3)	163(2)	[1]
4PicTu3Cl	39.6(1)	2.649(2)	141(2)	3.373(2)	155(2)	This work
4PicTuPh	24.3(3)	2.622(4)	146(3)	3.405(3)	159	[6]
4PicTu3OMe	6.7(1)	2.618(2)	147(2)	3.503(2)	152(2)	[30]
5PicTu3OMe	58.0(1)	2.687(2)	139(2)	3.386(2)	170(2)	[30]
5PicTu3Cl	56.8(1)	2.688(3)	141(3)	3.315(3)	169(3)	This work
5PicTuPh	28.8(1)	2.65(2)	140(5)	3.433(7)	156(5)	[6]
6PicTu3T	52.4(1)	2.637(4)	147(3)	3.420(3)	152(4)	[31]
6PicTuPh	11.2(7)	2.645(4)	146(3)	3.383(3)	167(3)	[6]
6PicTu3Cl	6.6(2)	2.610(6)	139(5)	3.424(6)	155(5)	This work
6PicTu3OMe	4.3(1)	2.608(4)	150(3)	3.431(3)	174(3)	[30]
4,6LutTu3T	45.2(3)	2.626(4)	143(2)	3.428(3)	166(2)	[31]
4,6LutTuPh	13.9(9)	2.629(4)	152(3)	3.461(2)	165(3)	[6]
4,6LutTu3OMe	4.9(1)	2.614(3)	147(3)	3.505(3)	166(2)	[30]
4,6LutTu3Cl	3.0(2)	2.643(9)	147(3)	3.466(4)	150(4)	[9]

Values of the angle between planes and their esd values have been rounded off for conformity.

3.3. NMR spectral studies

The ^{1}H NMR signals, Table 5, show little difference in chemical shift for the thioureas of this study. The downfield position of N3H is consistent with its involvement in intramolecular hydrogen bonding in solution.

Table 6
Melting points (°C), ΔH_{fus} values (kJ/mol) and selected ^{1}H NMR assignments for the various *N*-2-pyridyl-*N′*-3-chlorophenylthioureas

Thiourea	Melting point	ΔH_{fus}	N3H (N′H)	NH (N2H)	C6H	CH_3
PyTu3ClPh	184–185	39.8	13.68	8.44	8.06	
3PicTu3ClPh	123–124	26.6	14.10	8.26	8.09	2.61
4PicTu3ClPh	171–172	27.3	13.73	8.30	8.04	2.36
5PicTu3ClPh	185–187	24.0	14.60	8.18	7.93	2.42
6PicTu3ClPh	170–172	31.7	14.45	8.08		2.69
4,6LutTu3ClPh	174–175	30.9	14.22	8.41		2.40
						2.23

4. Conclusions

The significant differences in these thioureas are the large range of angles between the mean planes of the pyridyl and aryl rings, the positioning of the chloro substituent in 4PicTu3Cl and 5PicTu3Cl and the increase in the strength of the intramolecular N3H···N1 hydrogen bond accompanying a decrease in strength in the intermolecular N2H···S1 interaction. The ^{1}H NMR spectra are similar, but somewhat surprising is the lack of difference in the ΔH_{fus} values.

5. 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-179487 for PyTu3Cl, CCDC-190595 for 4PicTu3Cl, CCDC-179488 for 5PicTu3Cl, and CCDC-179489 for 6PicTu3Cl. Copies of available material can be

obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] D.X. West, A.K. Hermetet, L.J. Ackerman, J. Valdés-Martínez, S. Hernández-Ortega, Acta Crystallogr. C55 (1999) 811.
[2] J. Valdés-Martínez, S. Hernández-Ortega, D.X. West, L.J. Ackerman, J.K. Swearingen, A.K. Hermetet, J. Mol. Struct. 478 (1999) 219.
[3] E.A. Sudbeck, J.D. Jennissen, T.K. Venkatachalam, F.M. Uckun, Acta Crystallogr. C55 (1999) 2122.
[4] D.X. West, J.K. Swearingen, A.K. Hermetet, L.J. Ackerman, C. Presto, J. Mol. Struct. 522 (2000) 27.
[5] D.X. West, J.K. Swearingen, A.K. Hermetet, L.J. Ackerman, J. Mol. Struct. 562 (2001) 95.
[6] W. Kaminsky, K.I. Goldberg, D.X. West, J. Mol. Struct. 605 (2002) 9.
[7] L.F. Szczepura, K.K. Eilts, A.K. Hermetet, L.J. Ackerman, J.K. Swearingen, D.X. West, J. Mol. Struct. 607 (2002) 101.
[8] J. Valdés-Martínez, S. Hernández-Ortega, G. Espinosa-Pérez, C.A. Presto, A.K. Hermetet, K.D. Haslow, L.J. Ackerman, L.F. Szczepura, K.I. Goldberg, J.M. Giesen, W. Kaminsky, D.X. West, J. Mol. Struct. 608 (2002) 77.
[9] A.K. Hermetet, L.J. Ackerman, K.K. Eilts, T.K. Johnson, J.K. Swearingen, J.M. Giesen, K.I. Goldberg, W. Kaminsky, D.X. West, J. Mol. Struct. 605 (2002) 241.
[10] L.F. Szczepura, D.R. Kelman, A.K. Hermetet, L.J. Ackerman, K.I. Goldberg, K.A. Claborn, W. Kaminsky, D.X. West, J. Mol. Struct. 608 (2002) 245.
[11] D.R. Kelman, L.F. Szczepura, K.I. Goldberg, W. Kaminsky, A.K. Hermetet, L.J. Ackerman, J.K. Swearingen, D.X. West, J. Mol. Struct. 610 (2002) 143.
[12] D. Wassmaier, A. Kirfel, Acta Crystallogr. A51 (1995) 416.
[13] S. Mackay, C. Edwards, A. Henderson, C. Gilmore, N. Stewart, K. Shankland, A. Donald, MAXUS, version 2, University of Glascow, Scotland, 1997.
[14] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[15] L. Zsolnai, G. Huttner, ZORTEP, University of Heidelberg, Germany, 1994.
[16] A. Dago, M.A. Simonov, E.A. Pobedimskaya, A. Macias, A. Martín, Kristallografiya 32 (1987) 1024.
[17] A. Dago, M.A. Simonov, E.A. Pobedimskaya, A. Macias, A. Martín, Kristallografiya 33 (1988) 1021.
[18] A. Dago, Y. Shepelev, F. Fajardo, F. Alvarez, R. Pomés, Acta Crystallogr. C45 (1989) 1192.
[19] K.R. Koch, C. Sacht, S. Bourne, Inorg. Chim. Acta 232 (1995) 109.
[20] D.-C. Zhang, Y.-Q. Zhang, Y. Cao, B. Zhao, Acta Crystallogr. C52 (1996) 1716.
[21] Y. Cao, B. Zhao, Y.-Q. Zhang, D.-C. Zhang, Acta Crystallogr. C52 (1996) 1772.
[22] Y.-F. Yuan, S.-M. Ye, L.-Y. Zhang, B. Wang, Y.-M. Xu, J.-T. Wang, H.-G. Wang, Inorg. Chim. Acta 256 (1997) 313.
[23] Y.-F. Yuan, S.-M. Ye, L.-Y. Zhang, J.-T. Wang, H.-G. Wang, Polyhedron 16 (1997) 2271.
[24] A. Ramnathan, K. Sivakumar, K. Subramanian, N. Janarthanan, K. Ramadas, H.-K. Fun, Acta Crystallogr. C51 (1995) 2446.
[25] A. Ramnathan, K. Sivakumar, K. Subramanian, D. Meerarani, K. Ramadas, H.-K. Fun, Acta Crystallogr. C52 (1996) 139.
[26] A. Ramnathan, K. Sivakumar, N. Janarthanan, D. Meerarani, K. Ramadas, H.-K. Fun, Acta Crystallogr. C52 (1996) 411.
[27] A. Ramnathan, K. Sivakumar, K. Subramanian, N. Srinivasan, K. Ramadas, H.-K. Fun, Acta Crystallogr. C52 (1996) 656.
[28] A. Ramnathan, K. Sivakumar, K. Subramanian, N. Janarthanan, K. Ramadas, H.-K. Fun, Acta Crystallogr. C51 (1995) 1627.
[29] W. Kaminsky, D.R. Kelman, J.M. Giesen, K.I. Goldberg, K.A. Claborn, L.F. Szczepura, D.X. West, J. Mol. Struct. in press.
[30] J.M. Giesen, K.A. Claborn, K.I. Goldberg, W. Kaminsky, D.X. West, J. Mol. Struct. 613 (2002) 223.
[31] A.K. Hermetet, L.J. Ackerman, J.K. Swearingen, C.A. Presto, D.R. Kelman, J.M. Giesen, K.I. Goldberg, W. Kaminsky, D.X. West, J. Chem. Cryst. 32 (2002) 17.