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Structural, spectral and thermal studies of *N*-2-(4-picolyl)- and *N*-2-(6-picolyl)-*N′*-(2-chlorophenyl)thioureas and *N*-2-(6-picolyl)-*N′*-(2-bromophenyl)thiourea

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Abstract

N-2-(4-picolyl)-*N′*-2-chlorophenylthiourea, 4PicTu2Cl, monoclinic, $P2_1/c$, $a = 10.068(5)$, $b = 11.715(2)$, $c = 11.185(6)$ Å, $\beta = 96.88(4)°$, $V = 1309.8(2)$Å^3 and $Z = 4$; *N*-2-(6-picolyl)-*N′*-2-chlorophenylthiourea, 6PicTu2Cl, triclinic, *P*-1, $a = 7.4250(8)$, $b = 7.5690(16)$, $c = 12.664(3)$ Å, $\alpha = 105.706(17)$, $\beta = 103.181(13)$, $\gamma = 90.063(13)°$, $V = 665.6(2)$ Å^3 and $Z = 2$ and *N*-2-(6-picolyl)-*N′*-2-bromophenylthiourea, 6PicTu2Br, triclinic, *P*-1, $a = 7.512(4)$, $b = 7.535(6)$, $c = 12.575(4)$ Å, $a = 103.14(3)$, $\beta = 105.67(3)$, $\gamma = 90.28(4)°$, $V = 665.7(2)$ 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 position of the methyl substituent on the pyridine ring. The enthalpies of fusion and melting points of these thioureas are also affected. ^{1}H NMR studies in $CDCl_3$ show the NH′ hydrogen resonance considerably downfield from other resonances in their spectra.

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

1. Introduction

The crystal structure of *N*-(2-pyridyl)-*N′*-phenylthiourea [1] was reported following a ^{1}H NMR study of the intramolecular hydrogen bonding between the pyridyl nitrogen and N′H of *N*-(2-pyridyl)thioureas [2]. The intramolecular N′–H···N and intermolecular N–H···S hydrogen bonding, as well as the planarity of the molecules, have been the focus on more recent structural studies of substituted *N*-(2-pyridyl)-*N′*-arylthioureas [3–6]. 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 [7]. A study of the three *N*-2-(4,6-lutidyl)-*N′*-chlorophenylthioureas showed that *N*-2-(4,6-lutidyl)-*N′*-(2-chlorophenyl)thiourea could also be considered to be bifurcated [8]. Therefore, we decided to study the *N*-2-pyridyl- and *N*-2-picolyl-*N′*-(2-chlorophenyl)thioureas (Fig. 1) to determine whether other examples of bifurcated hydrogen bonding involving the chloro substituent exist. We also include *N*-2-(6-picolyl)-*N′*-(2-bromophenyl)thiourea, 6PicTu2Br, in this report.

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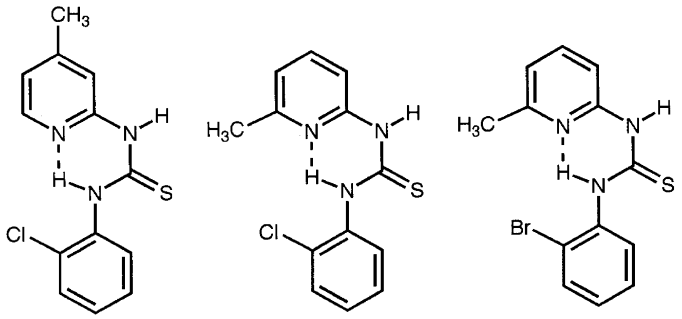

Fig. 1. Depiction of *N*-2-(4-picolyl)-*N′*-2-chlorophenylthiourea, 4PicTu2Cl; *N*-2-(6-picolyl)-*N′*-2-chlorophenylthiourea, 6PicTu2Cl and *N*-2-(6-picolyl)-*N′*-2-bromophenylthiourea, 6PicTu2Br.

Table 1
Crystallographic data and methods of data collection, solution and refinement for 4PicTu2Cl, 6PicTu2Cl and 6PicTu2Br

Crystal data	4PicTu2Cl	6PicTu2Cl	6PicTu2Br
Empirical formula	$C_{13}H_{12}ClN_3S$	$C_{13}H_{12}ClN_3S$	$C_{13}H_{12}BrN_3S$
Temperature	293(2)	293(2)	293(2)
Crystal color, habit	Colorless, prism	Colorless, prism	Colorless, prism
Crystal size (mm)	$0.26 \times 0.18 \times 0.14$	$0.30 \times 0.25 \times 0.18$	$0.16 \times 0.12 \times 0.10$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (#14)	P-1(#2)	*P*-1(#2)
a (Å)	10.068(5)	7.4250(8)	7.512(4)
b (Å)	11.715(2)	7.5690(16)	7.535(6)
c (Å)	11.185(6)	12.664(3)	12.575(4)
α (°)	90	105.706(17)	103.14(3)
β (°)	96.88(4)	103.181(13)	105.67(3)
γ (°)	90	90.063(13)	90.28(4)
Volume (Å^3)	1309.8(2)	665.6(2)	665.7(2)
Z	4	2	2
Formula weight	277.77	277.77	327.63
Density (calculated) (g/cm^3)	1.409	1.386	1.635
Absorption coefficient (mm^{-1})	0.435	0.428	0.323
F(000)	576	288	329
Index ranges	$0 \le h \le 11$	$0 \le h \le 9$	$0 \le h \le 7$
	$0 \le k \le 13$	$-9 \le k \le 9$	$-7 \le k \le 7$
	$-13 \le l \le 13$	$-16 \le l \le 15$	$-13 \le l \le 11$
θ Range for data collection	2.52–24.66	2.80–24.66	4.10–21.91
Total reflections	2467	2231	1579
Independent reflects. (R_{int}	1548, 0.0572	1671, 0.0135	1329, 0.0439
Absorption correction	Ψ-scan	Ψ-scan	Ψ-scan
Maximum and minimum transmissions	1.000 and 0.967	1.000 and 0.759	1.000 and 0.823
Goodness-of-fit	1.185	0.994	1.063
Largest diffraction peak (eÅ^{-3})	0.230	0.313	0.946
Largest diffraction hole (eÅ^{-3})	− 0.237	− 0.375	− 1.161
R_1, wR_2	0.0456, 0.1016	0.0394, 0.0917	0.614, 0.1564
R_1, wR_2 (all reflections)	0.0810, 0.1150	0.0627, 0.1104	0.0731, 0.1733

Table 2
Selected bond distances (Å) and angles (°) for 4PicTu2Cl, 6PicTu2Cl and 6PicTu2Br

	4PicTu2Cl	6PicTu2Cl	6PicTu2Br
Distances (Å)			
S1–C7	1.666(8), 1.674(6)	1.681(2)	1.687(7)
N1–C2	1.343(7), 1.311(13)	1.334(3)	1.332(8)
N1–C6	1.301(10), 1.340(7)	1.351(3)	1.353(9)
C2–N2	1.411(10), 1.427(7)	1.401(3)	1.419(9)
N2–C7	1.362(9), 1.359(11)	1.368(3)	1.351(8)
N3–C7	1.364(7), 1.358(12)	1.338(3)	1.334(8)
N3–C8	1.418(7), 1.417(10)	1.419(3)	1.415(9)
C9–Cl1(Br1)	1.738(6), 1.749(6)	1.748(3)	1.910(7)
Angles (°)			
C2–N1–C6	117.6(5), 117.4(8)	118.5(2)	118.4(6)
N1–C2–C3	122.4(7), 123.2(6)	123.2(2)	123.5(6)
N1–C2–N2	117.8(5), 119.0(8)	118.4(2)	118.0(5)
N2–C2–C3	119.7(5), 117.8(8)	118.4(2)	118.5(6)
C2–N2–C7	131.5(4), 129.8(9)	130.6(2)	130.6(6)
S1–C7–N2	119.0(4), 118.8(7)	119.34(19)	119.5(5)
N2–C7–N3	114.9(7), 115.8(5)	115.6(2)	115.6(6)
S1–C7–N3	126.0(5), 125.4(6)	125.02(19)	124.9(5)
C7–N3–C8	128.0(7), 130.8(5)	127.3(2)	126.9(6)
N3–C8–C9	116.2(5), 120.5(6)	119.1(2)	119.0(6)
N3–C8–C13	125.1(4), 120.8(9)	121.9(3)	121.6(6)

2. Experimental

2-Aminopyridine, the 2-aminopicolines and 2-chlorophenyl isothiocyanate, as well as 2-bromophenyl isothiocyanate, were purchased from Aldrich and used as received. 2-Aminopyridine or a 2-aminopicoline was mixed in a 1:1 molar ratio with 2-chlorophenyl isothiocyanate in 95% ethanol and the mixture stirred with warming for a minimum of 1 h. 6PicTu2Br was prepared by the same method using 2-amino-6-picoline and 2-bromophenyl isothiocyanate. 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 ΔHs 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°/min using a Perkin–Elmer differential scanning calorimeter, DSC7.

Table 3
Intramolecular and intermolecular hydrogen bond distances (Å) and angles (°) for 4PicTu2Cl, 6PicTu2Cl and 6PicTu2Br (italicized numbers are not 'hydrogen bonds')

Thiourea	D	A	D–H	H···A	D–H···A	∠(D–H···A)
Intramolecular						
4PicTu2Cl	N3	N1	0.93(9)	1.81(7)	2.628(10)	145(6)
	N3	Cl1	0.93(*9*)	2.63(*5*)	2.909(*4*)	98(*5*)
	N6	N4	1.03(7)	1.78(8)	2.642(7)	139(9)
	N6	Cl2	1.03(*7*)	2.46(*11*)	2.937(8)	107(*6*)
6PicTu2Cl	N3	N1	0.86(3)	1.95(3)	2.657(3)	139(3)
	N3	Cl1	0.86(*3*)	2.74(*3*)	2.957(*2*)	96(*2*)
6PicTu2Br	N3	N1	0.78(5)	1.97(6)	2.660(8)	148(5)
	N3	Br1	0.78(*5*)	2.89(*5*)	3.059(*6*)	95(*4*)
Intermolecular						
4PicTu2Cl[a]	N2	S1#1	0.93(5)	2.61(5)	3.441(4)	149(7)
	N5	S2#3	0.75(7)	2.75(8)	3.441(10)	155(7)
	C23	S2#3	0.90(9)	2.89(7)	3.654(10)	144(5)
	C31	S1#2	0.93(12)	2.95(13)	3.781(15)	149(8)
	C10	Cl1#5	0.95(5)	3.06(7)	3.647(8)	121(5)
	C11	S2#4	0.94(5)	2.97(5)	3.753(6)	142(4)
6PicTu2Cl[b]	N2	S1#1	0.76(3)	2.73(3)	3.463(3)	163(3)
	C3	S1#1	0.91(3)	2.79(3)	3.584(3)	147(2)
6PicTu2Br[c]	N2	S1#1	0.82(8)	2.74(8)	3.461(6)	149(6)
	C3	S1#1	0.94(8)	2.74(8)	3.592(8)	151(6)

[a] #1: $-x, -y, -1-z$; #2: $-1-x, -y, -1-z$; #3: $-x, -1-y, -z$; #4: $-1-x, -1-y, -1-z$; #5: $-1-x, -1-y, -1-z$.
[b] #1: $1-x, 1-y, -z$.
[c] #1: $-x, -1-y, -z$.

Table 4
Mean plane data and angles between planes for 4PicTu2Cl, 6PicTu2Cl and 6PicTu2Br

Compound	Plane	Plane #	Mean plane deviation	Atom with greatest deviation	Plane/plane	Angle
4PicTu2Cl	N1–C2–C3–C4–C5–C6	1	0.0080	C5, 0.0093(0.0058)	2/1	8.14(0.48)
	N2–C7–S1–N3	2	0.0111	C7, 0.0192(0.0058)	3/2	34.25(0.38)
	C8–C9–C10–C11–C12–C13	3	0.0142	C9, 0.0179(0.0047)	1/3	26.36(0.43)
	N4–C22–C23–C24–C25–C26	4	0.0016	C22, 0.0022(0.0059)	5/4	8.96(0.46)
	N5–C27–S2–N6	5	0.0016	C27, 0.0028(0.0065)	6/5	35.36(0.31)
	C28–C29–C30–C31–C32–C33	6	0.0079	C28, 0.0130(0.0042)	4/6	26.78(0.34)
6PicTu2Cl	N1–C2–C3–C4–C5–C6	1	0.0018	C4, 0.0030(0.0021)	2/1	13.80(0.12)
	N2–C7–S1–N3	2	0.0045	C7, 0.0077(0.0021)	3/2	50.39(0.08)
	C8–C9–C10–C11–C12–C13	3	0.0009	C9, 0.0013(0.0021)	1/3	47.37(0.07)
6PicTu2Br	N1–C2–C3–C4–C5–C6	1	0.0051	C4, 0.0087(0.0052)	2/1	15.16(0.28)
	N2–C7–S1–N3	2	0.0017	C7, 0.0029(0.0051)	3/2	50.92(0.17)
	C8–C9–C10–C11–C12–C13	3	0.0042	C8, 0.0056(0.0047)	1/3	47.49(0.17)

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 MACH 3 Diffractometer, Mo Kα ($\lambda = 0.71073$ Å) at 293 K. Cell constants and an orientation matrix for data collections were obtained by least squares refinements of the diffraction data from 25 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, were found on a difference Fourier map and refined isotropically. Scattering factors are from Waasmaier and Kirfel [9]. The structures were solved with MaXus [10], structure refinement was carried out with SHELXL-97 and the graphics used are Zortep [11]. Table 1 summarizes the crystal data, collection information and refinement data for these thioureas.

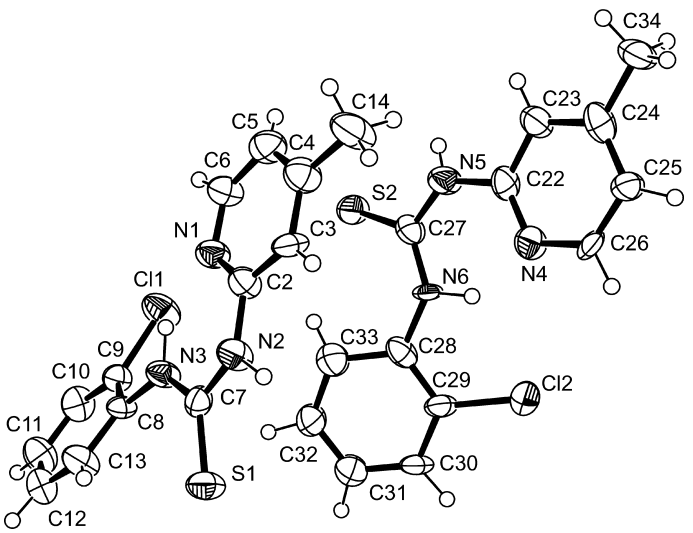

Fig. 2. ORTEP drawing showing the two unique molecules of 4PicTu2Cl with atom numbering scheme and displacement ellipsoids at 50% probability level.

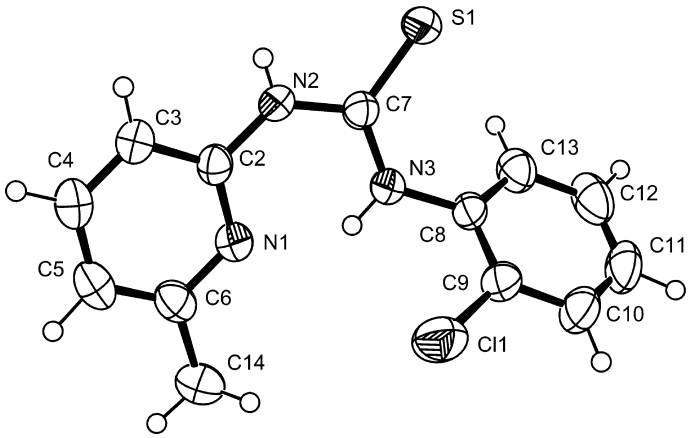

Fig. 3. ORTEP drawing of 6PicTu2Cl with atom numbering scheme and displacement ellipsoids at 50% probability level.

3. Results and discussion

3.1. Structural studies

Although a variety of solvents and solvent mixtures were tried, suitable crystals were obtained for only *N*-2-(4-picolyl)-*N′*-(2-chlorophenyl)thiourea, 4PicTu2Cl, and *N*-2-(6-picolyl)-*N′*-(2-chlorophenyl)thiourea, 6PicTu2Cl. Therefore, we were unable to obtain suitable crystals of *N*-2-pyridyl-, *N*-2-(3-picolyl)- and *N*-2-(5-picolyl)-*N′*-(2-chlorophenyl) thioureas, PyTu2Cl, 3PicTu2Cl and 5PicTu2Cl, respectively, but include the structure of 6PicTu2Br in this study. Bond distances and angles are listed in Table 2, the hydrogen bonding parameters are listed in Table 3 and the mean plane data in Table 4. Ortep drawings for 4PicTu2Cl, 6PicTu2Cl and 6PicTu2Br are shown in Figs. 2–4, respectively. Fig. 5 shows the intermolecular hydrogen bonding of 6PicTu2Cl to form the dimer characteristic of *N*-2-pyridyl-*N′*-arylthioureas [3–6,8].

Like other 2-pyridyl thioureas [1,3–8], 4PicTu2Cl, 6PicTu2Cl and 6PicTu2Br are found in a conformation resulting from intramolecular hydrogen bonding of N3H (N′H) to the pyridine nitrogen, N1. In addition, the halogen atom in each thiourea is positioned so that it could also interact with N3H, which will be discussed later in this article. Except for the bond to different halogen atoms, the bond distances are similar, Table 2. Further, the bond angles show very

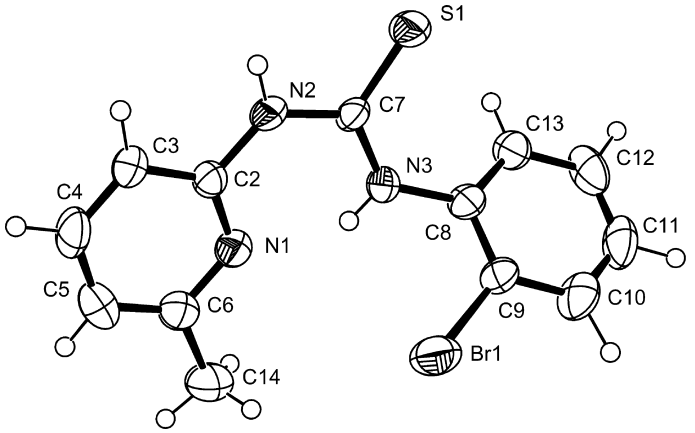

Fig. 4. ORTEP diagram showing 6PicTu2Br with atom numbering scheme and displacement ellipsoids at 50% probability level.

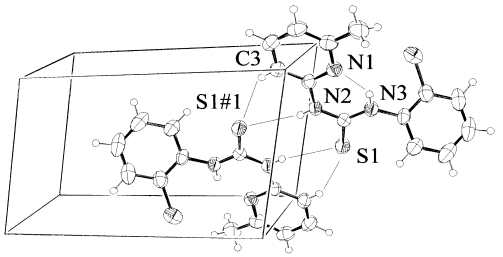

Fig. 5. Packing diagram of 6PicTu2Cl showing complementary N2–H···S1 and C3–H···S1 intermolecular interactions to form the dimer, as well as the N3–H···N1 intramolecular interaction.

little variation among the three thioureas; there is greater difference in the angles of the two unique molecules of 6PicTu2Cl than between the thioureas of this study. The bond distances and angles of these thioureas are also essentially the same as found for *N*-2-(4,6-lutidyl)-*N′*-(2-chlorophenyl)thiourea [8].

An intermolecular N2H2···S1 interaction is generally present in thioureas, Fig. 5, with intramolecular hydrogen bonding to an oxygen [12–19] or nitrogen atom [1,3–8], as well as thioureas without intramolecular hydrogen bonding [20–24]. The N2···S1 non-bonding distances show small differences for the present thioureas, but all three are larger than found for 4,6LutTu2Cl, 3.398(2) Å [8]. The small additional electronic effect of the second methyl group on the pyridine ring in 4,6LutTu2Cl results in a stronger intermolecular N2–H2···S1 interaction. In addition, the sulfur is located almost equally between N2 and C3 of the pyridine ring so that it also interacts with C3H3 in these thioureas, Fig. 5. The sulfur–hydrogen distances for the C3H3···S1 interactions are not much longer (i.e. ca. 0.15 Å) compared to the H3···S1 distances for the N2H2···S1 interactions. The only exception is a molecule of 4PicTu2Cl; the H3···S1 distance is greater than 3.0 Å. It should be noted that *N*-(3-picolyl)-*N′*-phenylthiourea, 3PicTuPh, in which the methyl group in the 3-position sterically hinders the N2–H2···S1 interaction, has a very long H2···S1 distance, 3.15 Å [25]. The comparatively low melting point and ΔH_{fus} (vide infra) for 3PicTu2Cl suggests a weaker intermolecular interaction and probably contributes to our inability to acquire a suitable crystal. Other C–H···X interactions in which a hydrogen is within less than 3.00 Å of X and the angle is above 110° are listed in Table 3.

For the intramolecular hydrogen bonding interaction, the non-bonding N3···N1 distances of the three thioureas of this study do not differ significantly. The angles for the N3–H3···N1 interaction are between 135 and 150°, the range found for previously studied thioureas attached to the pyridine ring [1,3–8,25]. The N3···X1 (X1 = Cl, Br) non-bonding distances are ca. 3.00 Å in contrast to the bifurcated *N*-2-pyridyl-*N′*-(2-methoxyphenyl)thioureas, which have N3···O distances ranging from ca. 2.56 to 2.62 Å [7]. However, the intermolecular N2···S non-bonding distances for *N*-2-pyridyl-*N′*-arylthioureas, as well as the present thioureas, Table 3, are often 3.4–3.5 Å. Assuming that a comparable distance for N3···X in hydrogen bonding interactions suggests that weak bifurcation is a possibility for these thioureas. However, because the N3–H3···X1 angles are less than 100° compared to ca. 106 for 4,6LutTu2Cl [8], the N3–H3···X interaction resulting in bifurcation is unlikely.

The data for the mean planes are shown in Table 4 and there is a difference in the planarity of the three molecules. The angle between the mean planes of the pyridyl and aryl ring, as a measure of planarity, is a

Table 5
Melting points (°C), ΔH_{fus} values (kJ/mol) and selected ^{1}H NMR assignments for the various *N*-2-pyridyl-, *N*-2-picolyl- and *N*-2-(4,6-lutidyl)-*N′*-2-chlorophenylthioureas

Thiourea	Mp	ΔH_{fus}	N3H (N′H)	NH (N2H)	C6H	CH_3	Reference
PyTu2Cl	156–157	28.3	13.91	8.24	7.48		[6]
3PicTu2Cl	126–128	11.2	14.33	8.10	7.74	2.59	This work
4PicTu2Cl	167–169	44.5	13.58	8.24	7.86	2.54	This work
5PicTu2Cl	186–188	24.2	14.01	8.18	8.00	2.43	This work
6PicTu2Cl	176–177	27.3	14.01	8.39		2.57	This work
4,6LutTu2Cl	193–195	42.2	14.11	8.26		2.39, 2.23	[9]

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 have been found to be less than 15° for the *N*-2-pyridyl- and *N′*-arylthioureas studied to date [1,3–8,25] although 6PicTu2Br has this angle just above 15°. 4PicTu2Cl is more planar than either 6PicTu2Cl or 6PicTu2Br, which are nearly identical. The angle between the pyridine rings in the two molecules of 4PicTu2Cl is 21.78(0.34)°, and it is the thiourea of this study that is the closest to having bifurcated hydrogen bonding, particularly the S2 molecule.

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 Table 5 along with their melting points. Values for *N*-(2-pyridyl)- and *N*-2-(4,6-lutidyl)-*N′*-2-chlorophenylthiourea, 4,6LutTu2Cl [8] are included. The low melting point and small value for the ΔH_{fus} for 3PicTu2Cl result from the 3-methyl group reducing the strength of the N–H···S interaction. Similarly, the ΔH_{fus} for *N*-2-(3-picolyl)-*N′*-phenylthiourea is 21.3 kJ/mol compared to 43.5 kJ/mol for *N*-2-(6-picolyl)-*N′*-phenylthiourea [25]. These data confirm that blocking the 3-methyl position of the pyridine ring reduces the strength of the intermolecular N2–H···S1 interaction and also, the weak C3–H···S1 interaction is absent.

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 N3*H* is consistent with its involvement in intramolecular hydrogen bonding in solution.

4. Conclusions

6PicTu2Cl and 6PicTu2Br are very similar structurally. The most significant differences for 4PicTu2Cl are the lack of a strong C3H3···S1 interaction accompanying the N2H2···S1 intermolecular interaction and its greater planarity compared to 6PicTu2Cl and 6PicTu2Br. The ^{1}H NMR spectra show that all of the thioureas of this study have N3H3···N1 intramolecular hydrogen bonding in chloroform solution. The very low values for the ΔH_{fus} and melting point for 3PicTu2Cl is consistent with results found for other 3-substituted *N*-2-pyridyl *N′*-phenylthioureas [23]. These compounds lack the strong intermolecular interaction, which makes it difficult to acquire suitable crystals for structural study. Finally, none of the present thioureas possesses a bifurcated intramolecular hydrogen bond based on the N3–H3–Cl1 angle being less than 100°.

4.1. 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-170606 for 4PicTu2Cl, CCDC-170607 for 6PicTu2Cl, and CCDC-170608 for 6PicTu2Br. 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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