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Structural, thermal and spectral studies of *N*-2-pyridyl-, *N*-2-picolyl- and *N*-2-(4,6-lutidyl)-*N*′-(3-methoxyphenyl)thioureas

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Abstract

N-2-pyridyl-*N*′-3-methoxyphenylthiourea, PyTu3OMe, triclinic, *P*-l, $a = 8.6590(16)$, $b = 8.7489(16)$, $c = 10.0540(15)$ Å, $\alpha = 90.255(9)$, $\beta = 66.765(8)$, $\gamma = 68.547(7)^\circ$, $V = 641.40(19)$ Å^3 and $Z = 2$; *N*-2-(3-picolyl)-*N*′-3-methoxyphenylthiourea, 3PicTu3OMe, triclinic, *P*-1, $a = 6.9100(9)$, $b = 12.7370(16)$, $c = 16.4710(14)$ Å, $\alpha = 107.782(6)$, $\beta = 91.656(7)$, $\gamma = 95.115(4)^\circ$, $V = 1372.5(3)$ Å^3 and $Z = 4$; *N*-2-(4-picolyl)-*N*′-3-methoxphenylthiourea, 4PicTu3OMe, monoclinic, *C*2/*c*, $a = 12.5036(7)$, $b = 8.5942(5)$, $c = 25.4050(10)$ Å, $\beta = 97.712(3)^\circ$, $V = 2705.3(2)$ Å^3 and $Z = 8$; *N*-2-(5-picolyl)-*N*′-3-methoxyphenylthiourea, 5PicTu3OMe, monoclinic, $P2_1/c$, $a = 10.9200(4)$, $b = 15.3920(15)$, $c = 8.1150(11)$ Å, $\beta = 92.020(5)^\circ$, $V = 1363.1(2)$ Å^3 and $Z = 4$; *N*-2-(6-picolyl)-*N*′-3-methoxyphenylthiourea, 6PicTu4OMe, triclinic, *P*-1, $a = 7.4220(16)$, $b = 9.944(3)$, $c = 10.038(3)$ Å, $\alpha = 104.815(9)$, $\beta = 94.452(16)$, $\gamma = 108.134(14)^\circ$, $V = 670.6(3)$ Å^3 and $Z = 2$ and *N*-2-(4,6-lutidyl)-*N*′-3-methoxyphenylthiourea, 4,6LutTu3OMe, orthorhombic, *Pbca*, $a = 16.3710(5)$, $b = 7.4910(6)$, $c = 24.1890(15)$ Å, $V = 2966.4(3)$, $Z = 8$. Intramolecular hydrogen bonding between N′H and the pyridine nitrogen and intermolecular hydrogen bonding between NH and the thione sulfur are characteristic of these thioureas except that 3PicTu3OMe has a very weak intermolecular NH···S interaction due to a steric effect of the methyl group. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 2-Pyridylthioureas; 3-Methoxyphenylthioureas; Crystal structures; Hydrogen bonding; Enthalpy of fusion

1. Introduction

Intramolecular hydrogen bonding between the pyridine nitrogen and N′H for *N*-(2-pyridyl)thioureas was confirmed some years ago by a ^{1}H NMR study [1]. More recently, the crystal structure of *N*-(2-pyridyl)-*N*′-phenylthiourea also showed intramolecular N′-H···N interaction in the solid state and demonstrated that intermolecular N–H···S hydrogen bonding [2] also existed and resulted in dimer formation. Both forms of hydrogen bonding, as well as the planarity of the molecules, have been the focus in recent structural studies of substituted *N*-(2-pyridyl)-*N*′-arylthioureas including *N*-(2-pyridyl)-*N*′-tolylthioureas [3] and the *N*-2-(4,6-lutidyl)-*N*′-tolylthioureas [4]. In addition, the structures of *N*-(5-bromo-2-pyridyl)-*N*′-2-(2,5-dimethoxyphenyethyl) thiourea [5] and four thioureas with *p*-substituted aryl groups including *N*-(2-pyridyl)-*N*′-(4-methoxyphenyl)thiourea [6], in which the methoxy oxygen is

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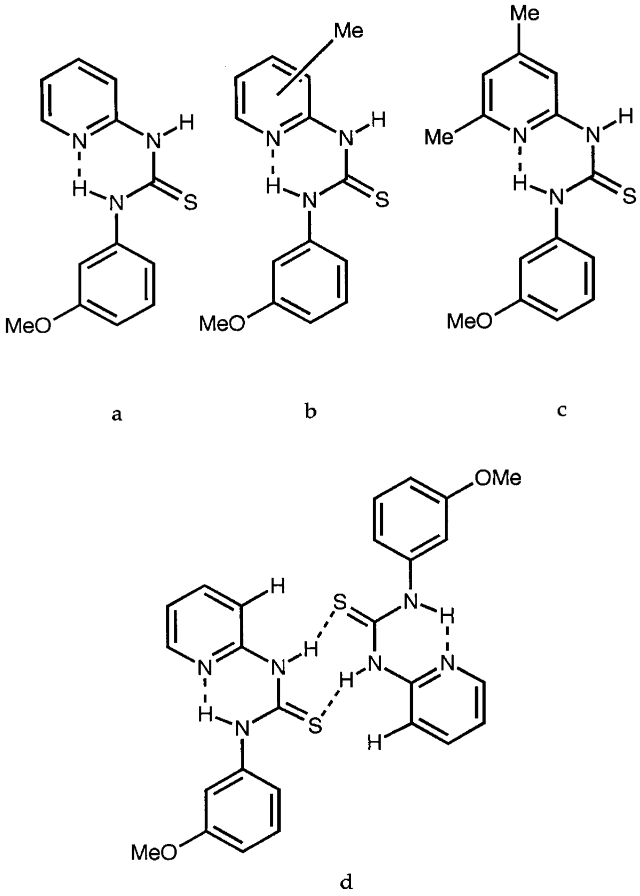

Fig. 1. Representation of (a) N-2-pyridyl-N'-3-methoxyphenylthiourea, (b) N-2-(n-picolyl)-N'-3-methoxyphenylthioureas, (c) N-2-(4,6-lutidyl)-N'-3-methoxyphenylthiourea and (d) a representation showing the intermolecular NH···S hydrogen bonding, as well as the potential C3H···S interaction.

also involved in weak intermolecular interactions, have been reported. A study of the structural, thermal and spectral properties of N-2-(picolyl)- and N-(4,6-lutidyl)-N'-phenylthioureas has been communicated [7]. A recent study showed that some members of a series of N-(2-pyridyl)-N'-2-methoxyphenylthioureas possess bifurcated intramolecular hydrogen bonding involving the pyridyl nitrogen and methoxy oxygen [8]. Since the methoxy substituent can add to the intermolecular interactions, we decided to prepare and characterize a series of N-2-pyridyl-N'-3-methoxyphenylthioureas. Included in this report are the X-ray crystal structures, ΔH_{fus} and selected ^{1}H NMR spectral assignments of N-2-pyridyl-, the four N-2-picolyl- and N-2-(4,6-lutidyl)-N'-3-methoxythioureas, Fig. 1, which are represented by the symbols PyTu3OMe (a), 3PicTu3OMe (b), 4PicTu3OMe (b), 5PicTu3OMe (b), 6PicTu3OMe (b) and 4,6LutTu3OMe (c).

2. Experimental

2.1. Preparative, spectral and thermal methods

3-Methoxyphenyl isothiocyanate and 2-aminopyridine, the four 2-aminopicolines and 2-amino-4,6-lutidine were purchased from Aldrich Chemical Company, Milwaukee, WI, and used as received. The desired 2-aminopyridine was mixed in a 1:1 molar ratio with 3-methoxyphenyl isothiocyanate in

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

Thiourea	M.p.	ΔH_{fus}	N′H (N3H)	NH (N2H)	C6H	OCH_3	CH_3
PyTu3OMe	136–138	22.2	13.60	8.20	7.74	3.85	2.19
3PicTu3OMe	88–89	19.3	13.94	8.10	7.54	3.85	2.18
4PicTu3OMe	159–160	26.4	13.61	8.21	7.74	3.85	2.18
5PicTu3OMe	180–181	34.5	13.60	8.27	8.03	3.84	2.17
6PicTu3OMe	172–173	31.5	14.60	7.87		3.84	2.18
4,6LutTu3OMe	165–166	33.1	14.27	8.07		3.84	2.19

95% ethanol and the mixture stirred with gentle warming for a minimum of 1 h. On cooling and slowly evaporating the reactant mixture, the thioureas crystallized from solution, were filtered and washed with *i*PrOH. The yields are ca. 70% for each of the thioureas and the melting points are listed in Table 6 with the ΔH_{fus} values. Their ^{1}H NMR spectra were recorded in $CDCl_3$ with a Varian 300 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.

2.2. X-ray data collection, structure solution and refinement

Crystals of the thioureas were grown by slow evaporation of 1:1 by volume acetone–ethanol mixtures at room temperature. The colorless thiourea crystals were mounted in random orientation on a glass fiber and data acquired with a Nonius Kappa CCD Diffractometer. 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 hydrogens attached to nitrogens and carbons, except for methyl groups, were found on a difference Fourier map and refined isotropically. Scattering factors are from Wassmaire and Kirfel [9], calculations were done by maXus, version 2.0 [10], structure refinement for the three thioureas was carried out with SHELXL-97 [11] and the graphics used are Zortep [12]. Tables 1 and 2 summarize the crystal data, collection information and refinement data for these thioureas.

3. Results and discussion

3.1. Structural studies

The ORTEP drawings for the thioureas are shown in Figs. 2–7 and bond distances and angles are listed in Table 3. These thioureas crystallize with one unique molecule per unit cell, except for 3PicTu3OMe, which has two crystallographically different molecules. In a similar study of the 2-methoxy analogues [8] we were not able to acquire a suitable crystal of *N*-2-(3-picolyl)-*N′*-2-methoxyphenylthiourea, 3PicTu2OMe, and only *N*-2-(6-picolyl)-*N′*-2-methoxyphenylthiourea, 6PicTu2OMe, has two crystallographically different molecules in the unit cell in that series. Like other *N*-2-pyridyl-*N′*-arylthioureas [2–8], the thioureas of this study are found in a conformation resulting from intramolecular hydrogen bonding of N3*H* (N′H) to the pyridine nitrogen, N1, in a manner similar to the benzoyl and acyl thioureas [13–20]. Some of these thioureas are nearly planar (vide infra), but evidently the packing of molecules causes 4PicTu3OMe to be unique in this series; it has its methoxy group on the same side of the molecule as the thione sulfur. This arrangement is also different from *N*-2-(4,6-lutidyl)-*N′*-3-chlorophenylthiourea, 4,6LutTu3Cl, which has its aryl ring rotated so that the chloro substituent is on the opposite side of the molecule from the thione sulfur. These thioureas have essentially the same bond distances, Table 3, except that the N3–C7 bond of PyTu3OMe is substantially shorter, 1.305(5) Å, than the analogous bond for the other thioureas of this study. There is a greater difference in the bond angles; for the various molecules some angles involving the thiourea moiety differ by 4–5°, Table 3.

The intramolecular hydrogen bonding parameters,

Table 1
Crystallographic data and methods of data collection, solution and refinement for PyTu3OMe, 3PicTu3OMe and 4PicTu3OMe

Crystal data	PyTu3OMe	3PicTu3OMe	4PicTu3OMe
Empirical formula	$C_{13}H_{13}ON_3S$	$C_{14}H_{15}ON_3S$	$C_{14}(H_{15}ON_3S$
Crystal color, habit	Colorless, prism	Pale yellow, prism	Colorless, prism
Crystal size (mm)	0.26 × 0.12 × 0.10	0.48 × 0.31 × 0.24	0.48 × 0.48 × 0.41
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1 (#2)	*P*-1 (#2)	*C*2/*c*
a (Å)	8.6590(16)	6.9100(9)	12.5040(7)
b (Å)	8.7489(16)	12.7370(16)	8.5940(5)
c (Å)	10.0540(15)	16.4710(14)	25.4050(10)
α (°)	90.255(9)	107.782(6)	90
β (°)	66.765(8)	91.656(7)	97.712(3)
γ (°)	68.547(7)	95.115(4)	90
Volume (Å^3)	641.40(19)	1372.5(3)	2705.3(2)
Z	2	4	8
Formula weight	259.32	273.35	273.35
Density (calcd) (g/cm^3)	1.343	1.323	1.342
Absorption coefficient (mm^{-1})	0.244	0.231	0.235
Reflections for indexing	152	489	182
θ range for data collection (°)	4.15–21.96	3.54–21.96	3.24–28.30
F(000)	272	576	1152
Index ranges	$-9 \leq h \leq 9$	$-7 \leq h \leq 6$	$0 \leq h \leq 16$
	$-9 \leq k \leq 9$	$-13 \leq k \leq 13$	$-10 \leq k \leq 11$
	$-10 \leq l \leq 10$	$-17 \leq l \leq 16$	$-28 \leq l \leq 28$
Reflections collected	2078	5131	4584
Inddpendent reflections, R_{int}	1032, 0.1068	3119, 0.0474	2928, 0.0285
Completeness to θ (%)	83.6	92.6	40.7
Absorption correction	HKL-SCALEPACK	HKL-SCALEPACK	HKL-SCALEPACK
Max. and min. transmissions	0.9761 and 0.9394	0.9466 and 0.8971	0.9099 and 0.8957
Goodness-of-fit	0.948	0.990	1.049
Largest diff. Peak, hole (eÅ^{-3})	0.221, −0.186	0.271, −0.156	0.206, −0.201
R, wR_2	0.0563, 0.1194	0.0542, 0.1332	0.0437, 0.1189
R, wR_2 (all reflections)	0.0930, 0.1337	0.0975, 0.1545	0.0704, 0.1315

Table 4, for this series of thioureas are in the range found for previously studied *N*-2-pyridyl-*N*′-arylthioureas [2–8]. The present thioureas can be separated into two groups of three in terms of the non-bonding N3···N1 distance; PyTu3OMe, 3PicTu3OMe and 5PicTu3OMe average ca. 2.67 Å while 4PicTu3OMe, 6PicTu3OMe and 4,6LutTu3OMe average ca. 2.61 Å. A similar grouping occurs for the H3···N1 distances, and therefore, the methyl groups in the 4- and 6-positions (i.e. *ortho* and *para* to the pyridine nitrogen) strengthen this interaction by donation of electron density. This also indicates that the methyl group in the 6-position of the pyridine ring does not exert a significant steric effect. Both distances for the two groups fall in the range found for other substituted *N*-2-pyridyl-*N*′-arylthioureas [2–8]. Except for PyTu3OMe, the N3H3–N1 angles for the present thioureas are between 135 and 150° in agreement with the those found for previously studied *N*-2-pyridyl-*N*′-arylthioureas [2–8].

The intermolecular N2H2···S1 interaction, Fig. 1(d), is present in thioureas with intramolecular hydrogen bonding to an oxygen [13–20] or nitrogen atom [2–8], as well as thioureas without intramolecular hydrogen bonding [21–25]. The N2···S1 non-bonding distances show small differences for the present thioureas, and generally, those thioureas with the stronger intramolecular hydrogen bonding have longer N2···S1 distances. For example, in 6PicTu3OMe, N3···N1 is 2.608(4) Å and N2···S1 is 3.431(3) Å, and in 5PicTu3OMe N3···N1 is 2.687(2) Å and N2···S1 is 3.386(2) Å. The H2···S1

Table 2
Crystallographic data and methods of data collection, solution and refinement for 5PicTu3OMe, 6PicTu3OMe and 4,6LuTu3OMe

Crystal data	5PicTu3OMe	6PicTu3OMe	4,6LutTu3OMe
Empirical formula	$C_{14}H_{15}ON_3S$	$C_{14}H_{15}ON_3S$	$C_{15}H_{17}ON_3S$
Crystal color, habit	Colorless, plate	Colorless, prism	Colorless, prism
Crystal size (mm)	1.03 × 0.96 × 0.12	0.24 × 0.19 × 0.10	0.29 × 0.24 × 0.14
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$ (#14)	P-1 (#2)	$Pbca$ (#61)
a (Å)	10.9200(4)	7.4220(16)	16.3710(5)
b (Å)	15.3920(15)	9.944(3)	7.4910(6)
c (Å)	8.1150(11)	10.038(3)	24.1890(15)
α (°)	90(0)	104.815(9)	90(0)
β (°)	92.020(5)	94.452(16)	90(0)
γ (°)	90(0)	108.134(14)	90(0)
Volume (Å^3)	1363.1(2)	670.6(3)	2966.4(3)
Z	4	2	8
Formula weight	273.35	273.35	287.37
Density (calcd) (g/cm^3)	1.332	1.354	1.291
Absorption coefficient (mm^{-1})	0.233	0.237	0.218
Reflections for indexing	191	270	210
θ range for data collection (°)	3.35–26.36	3.53–26.31	3.00–26.37
F(000)	576	288	1224
Index ranges	$-13 \le h \le 13$	$-8 \le h \le 8$	$-20 \le h \le 20$
	$-19 \le k \le 17$	$-12 \le k \le 11$	$-9 \le k \le 9$
	$-8 \le l \le 8$	$-11 \le l \le 12$	$-30 \le l \le 30$
Reflections collected	7305	3790	5327
Independent reflections, R_{int}	6468, 0.0418	2423, 0.0894	2990, 0.0670
Completeness to θ (%)	89.5	89.0	86.6
Absorption correction	HKL-SCALEPACK	HKL-SCALEPACK	HKL-SCALEPACK
Max. and min. transmissions	0.9726 and 0.7954	0.9767 and 0.9454	0.9702 and 0.9396
Goodness-of-fit	0.932	0.838	0.826
Data/restaints/parameters	2596/0/210	2423/0/211	2990/0/216
Largest diff. peak, hole, e (Å^{-3})	0.130, −0.232	0.205, −0.220	0.196, −0.177
Extincton coefficient	0.015(5)	0.055(11)	None
R, wR_2	0.0410, 0.0920	0.0535, 0.1539	0.0466, 0.1100
R, wR_2 (all reflections)	0.0895, 0.1056	0.0990, 0.1226	0.1346, 0.1359

distance in one of the two molecules of 3PicTu3OMe is ca. 3.28 Å, and this distance is longer in the second molecule making both considerably longer than the other molecules of this study (and outside the arbitrary 3.0 Å we required for listing in Table 4). Therefore, the steric effect of the methyl group in the 3-position hinders the N2–H2···S1 interaction that is common to most thioureas. There are CH···X interactions (i.e. H···S distances <3.00 Å) listed in Table 3 for 3PicTu3OMe that partially make up for the absence of a strong N2H2···S1 interaction. Like other N-2-pyridyl-N'-arylthioureas [6–8,26,27], other than 3PicTu3OMe, the rest of these thioureas have a weak interaction, C3H3···S1; S1 is positioned almost equally between C3 and N2 of another molecule, Fig. 1(d). The C3H···S1 interactions when compared to N2H···S1 are the following: C3···S1 is longer by 0.14–0.30 Å, H···S1 is longer by 0.19–0.44 Å, and the angle C3–H···S1 is smaller by 14–34°. These ranges are comparable to previously studied to N-2-pyridyl-N'-arylthioureas [6–8,26,27]. Other weak C–H···X interactions are listed in Table 3; only the bulkiest member of the series, 4,6LutTu3OMe, did not have a significant interaction by its methoxy oxygen.

The data for the mean planes are shown in Table 5, and there is substantial difference in the planarity of these thioureas. The angle between the mean planes of the pyridyl and aryl rings, as a measure of planarity, is a useful parameter. The choice of this angle is most

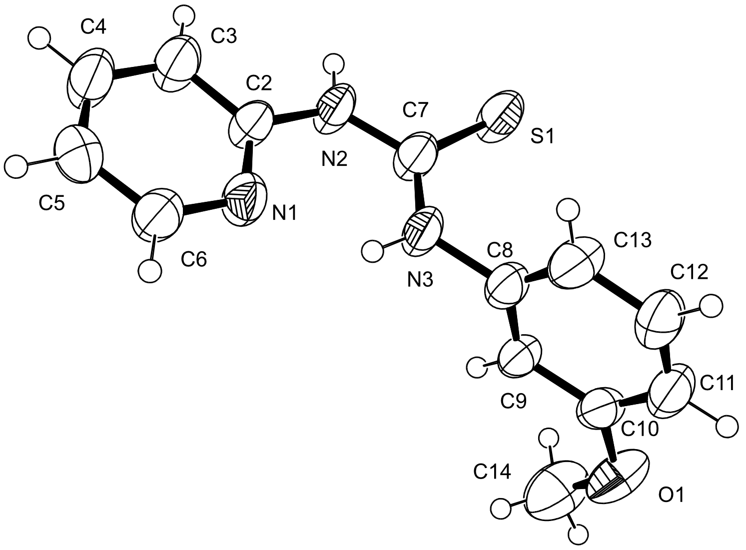

Fig. 2. ORTEP drawing showing PyTu3OMe with atom numbering scheme and displacement ellipsoids at 50% probability level.

useful since the angle between the mean planes of the pyridine ring and the thiourea moiety does not show large variation, 2–11°, like other *N*-2-pyridyl-*N*′-arylthioureas studied to date [2–8,26,27]. In PyTu3OMe the angle between the pyridine and aryl planes is essentially 90°, and it is less than 5° for 6PicTu3OMe and 4,6LutTu3OMe. Therefore, the position and presence of methyl groups on the pyridine ring affects the packing of these molecules resulting in large differences in their planarity.

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 6 along with their melting points. The low value for 3PicTu3OMe is due to the 3-methyl group substantially 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 [7], *N*-2-(3-picolyl)-*N*′-4-tolylthiourea is 22.5 kJ/mol [26], and that of *N*-2-(3-picolyl)-*N*′-4-chlorophenylthiourea

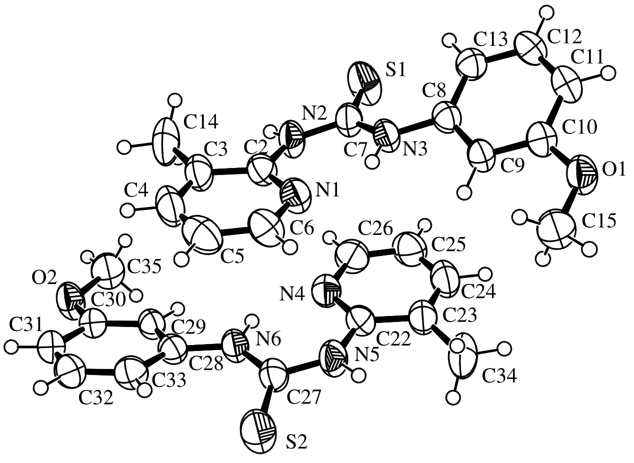

Fig. 3. ORTEP drawing of the four unique molecules of 3PicTu3OMe with atom numbering scheme and displacement ellipsoids at 50% probability level.

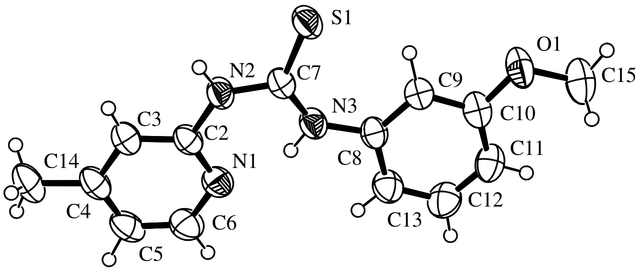

Fig. 4. ORTEP diagram showing 4PicTu3OMe with atom numbering scheme and displacement ellipsoids at 50% probability level.

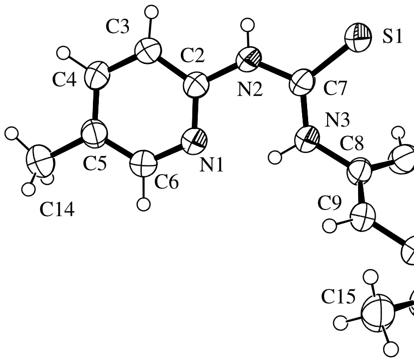

Fig. 5. ORTEP diagram showing 5PicTu3OMe with atom numbering scheme and displacement ellipsoids at 50% probability level.

is 16.1 kJ/mol [28]. These values are substantially lower than analogues with methyl groups on other positions of the pyridine ring, as well as without a methyl group on the ring. These data confirm that blocking the 3-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.

Even though there are weak intermolecular interactions with the methoxy oxygen, it is significant that these 3-methoxythioureas generally have lower ΔH_{fus} values than thioureas with methyl substituents on either or both rings. This indicates that the weak hydrogen bonding interactions are not as important as the N2H···S1 intermolecular interaction, and possibly the accompanying C3H···S1 interaction in thioureas prepared from substituted 2-aminopyridines. The melting points listed in the Table 6 are consistent with these same conclusions.

3.3. NMR spectral studies

The ^{1}H NMR signals, Table 6, show little change in chemical shift for the thioureas of this study except for N3H ($N'H$), which is in a downfield position consistent

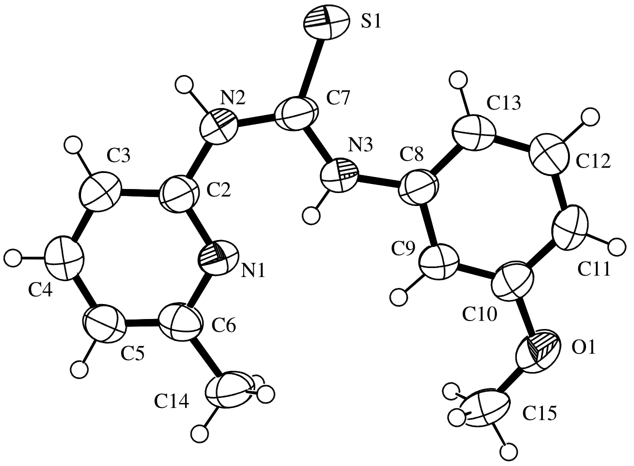

Fig. 6. ORTEP diagram showing 6PicTu3OMe with atom numbering scheme and displacement ellipsoids at 50% probability level.

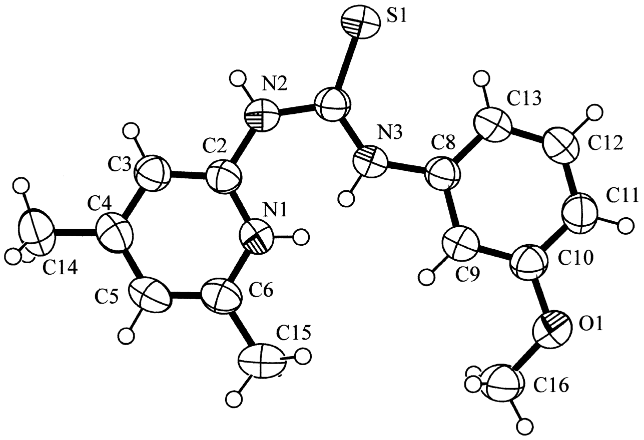

Fig. 7. ORTEP diagram showing 4,6LutTu3OMe with atom numbering scheme and displacement ellipsoids at 50% probability level.

Table 3
Selected bond distances (Å) and angles (°) for PyTu3OMe, 3PicTu3OMe, 4PicTu3OMe, 5PicTu3OMe, 6PicTu3OMe and 4,6LuTu3OMe

	PyTu3OMe	3PicTu3OMe[a]		4PicTu3OMe	5PicTu3OMe	6PicTu3OMe	4,6LuTu3OMe
Distances (Å)							
S1–C7	1.690(4)	1.664(3)	1.669(3)	1.6761(17)	1.6793(19)	1.679(3)	1.671(2)
N1–C2	1.321(5)	1.334(4)	1.331(4)	1.329(2)	1.328(2)	1.334(4)	1.333(3)
N1–C6	1.350(5)	1.335(5)	1.347(5)	1.339(2)	1.347(2)	1.352(4)	1.345(3)
N2–C2	1.393(5)	1.399(4)	1.395(4)	1.401(2)	1.393(2)	1.398(4)	1.403(3)
N2–C7	1.368(5)	1.376(4)	1.372(4)	1.378(2)	1.359(2)	1.377(4)	1.377(3)
N3–C7	1.305(5)	1.336(4)	1.336(4)	1.336(2)	1.331(2)	1.338(4)	1.338(3)
N3–C8	1.437(5)	1.410(4)	1.406(4)	1.407(2)	1.434(2)	1.413(4)	1.410(3)
C10–O1	1.372(5)	1.370(4)	1.370(4)	1.377(2)	1.367(3)	1.378(4)	1.373(3)
O1–C15	1.420(7)[a]	1.406(4)	1.417(4)	1.428(2)	1.412(3)	1.422(4)	1.422(3)[b]
Angles (°)							
C2–N2–C7	129.8(4)	131.9(3)	132.4(3)	130.72(16)	131.22(18)	130.5(3)	130.8(2)
C7–N3–C8	124.4(4)	131.1(3)	131.9(3)	133.10(15)	125.17.(16)	133.3(3)	132.9(2)
N1–C2–N2	118.6(4)	117.9(3)	118.2(3)	118.47(15)	119.17(17)	117.9(3)	118.5(2)
N2–C2–C3	118.8(4)	118.6(3)	117.7(3)	118.80(17)	118.51(17)	119.4(3)	118.7(2)
S1–C7–N2	118.1(3)	118.0(3)	117.2(3)	117.85(13)	118.65(15)	118.1(2)	118.0(2)
S1–C7–N3	123.6(3)	127.3(3)	127.6(3)	127.48(13)	124.03(15)	126.7(3)	127.6(2)
N2–C7–N3	118.3(4)	114.7(3)	115.2(3)	114.67(14)	117.32(17)	115.2(3)	114.4(2)
N3–C8–C9	118.7(5)	115.5(3)	115.5(3)	114.52(15)	118.21(18)	114.2(3)	114.1(2)
N3–C8–C13	119.4(5)	124.5(3)	125.3(3)	125.74(16)	120.5(2)	125.7(3)	126.2(2)
C9–C10–O1	122.8(5)	124.3(3)	124.8(3)	114.53(16)	123.8(2)	125.0(3)	124.5(2)
C11–C10–O1	115.6(4)	115.2(3)	115.0(3)	124.05(17)	116.43(19)	114.3(3)	115.0(3)
C10–O1–C15	119.1(4)[a]	117.7(3)	117.5(3)	117.61(16)	117.01(17)	117.4(3)	117.8(2)[c]

[a] The second column represents the analogous bonds in the S2 molecule.

[b] O1–C16.

[c] C10–O1–C16.

Table 4
Intramolecular and intermolecular hydrogen bond distances (Å) and angles (°) for PyTu3OMe, 3PicTu3OMe, 4PicTu3OMe, 5PicTu3OMe, 6PicTu3OMe, and 4,6LutTu3OMe, as well as C–H···X interactions with H···X distances of less than 3.00 Å

Thiourea	D	A	D–H	H···A	D–H···A	∠(D–H···A)
Intramolecular						
PyTu3OMe	N3	N1	0.87(4)	2.00(5)	2.657(4)	132(4)
3PicTu3OMe	N3	N1	0.83(3)	1.93(3)	2.658(4)	145(3)
	N6	N4	0.83(3)	1.96(4)	2.672(4)	143(3)
4PicTu3OMe	N3	N1	0.88(2)	1.832(19)	2.6178(19)	147(2)
5PicTu3OMe	N3	N1	0.877(17)	1.96(2)	2.687(2)	139.2(17)
6PicTu3OMe	N3	N1	0.86(3)	1.82(3)	2.608(4)	150(3)
4,6Lut3OMe	N3	N1	0.88(3)	1.83(3)	2.614(3)	147(3)
Intermolecular						
PyTu3OMe[a]	N2	S1#1	0.74(3)	2.73(3)	3.410(4)	153(3)
	C3	S1#1	0.93(4)	2.92(4)	3.666(5)	139(3)
	C6	O1#2	1.02(4)	2.86(5)	3.622(6)	132(4)
	C6	O1#3	1.02(4)	2.75(5)	3.447(6)	126(3)
	N3	O1#3	0.87(4)	2.79(4)	3.512(5)	142(4)
3PicTu3OMe[b]	C34	O1#1	0.96	2.50	3.426(5)	163.1
	C15	O1#1	0.96	2.91	3.611(5)	130.7
	C14	O2#1	0.96	2.51	3.383(5)	150.5
	C14	S1#3	0.96	2.93	3.870(5)	167.3
4PicTu3OMe[c]	N2	S1#1	0.86(2)	2.72(2)	3.5025(16)	151.9(18)
	C3	S1#1	0.85(3)	2.99(2)	3.641(2)	135(2)
	C11	O1#3	0.900(19)	2.82(2)	3.493(2)	132.2(15)
	C15	O1#2	0.96	2.89	3.711(3)	144.6
5PicTu3OMe[d]	N2	S1#1	0.80(2)	2.60(2)	3.386(2)	169.5(18)
	C3	S1#1	0.92(2)	2.81(2)	3.619(2)	147.8(16)
	C4	O1#2	0.96(2)	2.73(2)	3.600(3)	150.8(16)
	C6	N3#3	0.98(2)	2.94(2)	3.819(3)	148.8(16)
	C15	S1#3	0.96	2.91	3.706(2)	140.7
	C15	O1#4	0.96	2.84	3.679(3)	146.1
6PicTu3OMe[e]	N2	S1#1	0.93(4)	2.51(4)	3.431(3)	174(3)
	C3	S1#1	0.94(3)	2.96(3)	3.732(4)	140(3)
	C4	O1#2	0.93(4)	2.89(4)	3.746(5)	154(3)
	C11	O1#3	0.90(4)	2.91(4)	3.569(5)	131(3)
	C14	N3#4	0.96	2.87	3.531(5)	126.8
4,6Lut3OMe[f]	N2	S1#1	0.84(3)	2.68(3)	3.505(3)	166(2)
	C3	S1#1	0.96(3)	2.89(2)	3.759(3)	151.3(19)

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

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

[c] #1: $0.5-x, -0.5-y, 1-z$; #2: $0.5-x, 0.5+y, 1.5-z$.

[d] #1: $2-x, -y, -z$; #2: $-1+x, 0.5-y, 0.5+z$; #3: $x, 0.5-y, 0.5+z$; #4: $3-x, 1-y, -z$.

[e] #1: $1-x, -1-y, 1-z$; #2: $x, -1+y, -1+z$; #3: $2-x, 1-y, 2-z$; #4: $2-x, -y, 1-z$.

[f] #1: $2-x, -y, 1-z$.

with its involvement in intramolecular hydrogen bonding in solution. The presence of a methyl group in the 6-position on the pyridine ring (i.e. 6PicTu3OMe and 4,6LutTu3OMe) provides sufficient additional electron density to shift the N3*H* resonance further downfield compared to other thioureas of this study, Table 6. This same effect was found when comparing the various *N*-2-picolyl-*N*′-phenylthioureas and for *N*-2-(4,6-lutidyl)-*N*′-phenylthiourea [7]. Also, N2*H* is somewhat upfield for thioureas with a 6-methyl group in this series, as well as in the previous series [7].

4. Conclusions

The hydrogen bonding interactions are similar to those of related *N*-2-pyridyl-*N*′-arylthioureas. The

Table 5
Mean plane data and angles between planes for PyTu3OMe, 3PicTu3OMe, 4PicTu3OMe, 5PicTu3OMe, 6PicTu3OMe and 4,6LutTu3OMe

Compound	Plane	Plane	Mean plane deviation	Atom with greatest deviation	Plane/Plane	Angle
PyTu3OMe	N1–C2–C3–C4–C5–C6	1	0.0056	C2, 0.0092(0.0035)	2/1	2.66(0.35)
	N2–C7–S1–N3	2	0.0000	C7, 0.0001(0.0038)	3/2	88.17(0.12)
	C8–C9–C10–C11–C12–C13	3	0.0073	C9, 0.0098(0.0028)	1/3	89.68(0.13)
3PicTu3OMe	N1–C2–C3–C4–C5–C6	1	0.0077	C3, 0.0118(0.0025)	2/1	10.11(0.08)
	N2–C7–S1–N3	2	0.0059	C7, 0.0102(0.0029)	3/2	29.64(0.07)
	C8–C9–C10–C11–C12–C13	3	0.0029	C12, 0.0050(0.0025)	1/3	32.40(0.08)
	N4–C22–C23–C24–C25–C26	4	0.0078	C23, 0.0124(0.0024)	5/4	3.25(0.09)
	N5–C27–S2–N6	5	0.0026	C27, 0.0046(0.0029)	6/5	18.40(0.10)
	C28–C29–C30–C31–C32–C33	6	0.0066	C31, 0.0097(0.0025)	4/6	15.72(0.10)
4PicTu3OMe	N1–C2–C3–C4–C5–C6	1	0.0061	N1, 0.0096(0.0012)	2/1	4.48(0.11)
	N2–C7–S1–N3	2	0.0008	C7, 0.0014(0.0013)	3/2	10.93(0.11)
	C8–C9–C10–C11–C12–C13	3	0.0022	C8, 0.0033(0.0012)	1/3	6.67(0.12)
5PicTu3OMe	N1–C2–C3–C4–C5–C6	1	0.0029	C6, 0.0040(0.0015)	2/1	2.86(0.12)
	N2–C7–S1–N3	2	0.0030	C7, 0.0051(0.0017)	3/2	59.82(0.07)
	C8–C9–C10–C11–C12–C13	3	0.0045	C8, 0.0074(0.0013)	1/3	57.95(0.07)
6PicTu3OMe	N1–C2–C3–C4–C5–C6	1	0.0050	C2, 0.0081(0.0021)	2/1	2.38(0.12)
	N2–C7–S1–N3	2	0.0037	C7, 0.0064(0.0025)	3/2	5.57(0.11)
	C8–C9–C10–C11–C12–C13	3	0.0058	C12, 0.0085(0.00	1/3	4.32(0.11)
4,6LutTu3OMe	N1–C2–C3–C4–C5–C6	1	0.0026	N1, 0.0042(0.0016)	2/1	3.76(0.11)
	N2–C7–S1–N3	2	0.0016	C7, 0.0028(0.0020)	3/2	8.44(0.11)
	C8–C9–C10–C11–C12–C13	3	0.0053	C13, 0.0085(0.0022)	1/3	4.92(0.10)

difference in the planarity among these thioureas is an important aspect of their solid state properties and results from the number and position of methyl substituents causing different packing effects. The very low values for ΔH_{fus} and melting point for 3PicTu3OMe result from the steric effect of the 3-methyl group weakening the intermolecular N2–H···S1 interaction. This is consistent with results found for other *N*-2-(3-substituted) pyridyl *N*′-arylthioureas [7,26,28].

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-168211 for PyTu3OMe, CCDC-168212 for 3Pic-Tu3OMe, CCDC-168213 for 4PicTu3OMe, CCDC-168214 for 5PicTu3OMe, CCDC-168215 for 6Pic-Tu3OMe and CCDC-168216 for 4,6LutTu3OMe. 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, e-mail: deposit@ccdc.cam.ac.uk).

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