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# Spectral and structural studies of N-(2)-pyridylethyl-N'-arylthioureas

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### Abstract

*N*-(2-pyridylethyl)-*N'*-phenylthiourea, triclinic, P-1, a = 8.616(1) Å, b = 9.663(1) Å, c = 9.761(1) Å,  $\alpha = 102.05(1)^{\circ}$ ,  $\beta = 102.36(1)^{\circ}$ , and  $\gamma = 116.17(1)^{\circ}$ , V = 668.5(1) Å<sup>3</sup>, Z = 2,  $\mu = 2.022$  mm<sup>-1</sup>, *N*-(2-pyridylethyl)-*N'*-*p*-tolylthiourea, triclinic, P-1, a = 8.804(3) Å, b = 9.951(2) Å, c = 10.255(2) Å,  $\alpha = 115.03(2)^{\circ}$ ,  $\beta = 105.93(2)^{\circ}$ ,  $\gamma = 104.04(2)^{\circ}$ , V = 713.43(1) Å<sup>3</sup>, Z = 2,  $\mu = 2.173$  mm<sup>-1</sup>, *N*-(2-pyridyl-ethyl)-*N'*-*p*-bromophenylthiourea, triclinic, P-1, a = 9.536(1) Å, b = 9.809(1) Å, c = 10.042(2) Å,  $\alpha = 115.88(1)^{\circ}$ ,  $\beta = 96.80(1)^{\circ}$ , and  $\gamma = 110.44(1)^{\circ}$ , V = 750.0(6) Å<sup>3</sup>, Z = 2,  $\mu = 28.73$  mm<sup>-1</sup>, *N*-(2-pyridyl-ethyl)-*N'*-*p*-nitrophenylthiourea, triclinic, P-1, a = 8.046(2) Å, b = 8.602(3) Å, c = 10.938(3) Å,  $\alpha = 80.74(3)^{\circ}$ ,  $\beta = 89.77(2)^{\circ}$ ,  $\gamma = 77.00(3)^{\circ}$ , V = 727.6(6) Å<sup>3</sup>, Z = 2,  $\mu = 2.325$  mm<sup>-1</sup> and *N*-(2-pyridylethyl)-*N'*-*p*-methoxyphenylthiourea, monoclinic, P2<sub>1</sub>/n, a = 11.526(2) Å, b = 9.723(2) Å, c = 13.460(2) Å,  $\beta = 100.49(2)^{\circ}$ , V = 1483.3(2) Å<sup>3</sup>, Z = 4,  $\mu = 1.929$  mm<sup>-1</sup>. All five molecules possess an intramolecular hydrogen bond between NH and the pyridyl nitrogen, as well as intermolecular hydrogen bonding between N'H and a thione sulfur of a second molecule to form centrosymmetric dimers. Solution <sup>1</sup>H NMR studies (CDCl<sub>3</sub>) show the N'H resonance downfield for each thiourea and its shift, as well as that of NH, is affected by substituents on the phenyl ring. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thioureas; Hydrogen bonding; Crystal structure; N-pyridylethylthioureas

# 1. Introduction

Although <sup>1</sup>H NMR has correctly predicted intramolecular hydrogen bonding involving the pyridyl nitrogen and N'H for N-(2-pyridyl)-N'-phenylthiourea [1], only recently has a structural study been reported [2]. Other examples of substituted N-(2-pyridyl)-N'arylthioureas (i.e. substituents on the pyridyl and/or

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aryl rings) have been characterized structurally and spectroscopically [3,4]. Intermolecular NH hydrogen bonding with a sulfur of a neighboring molecule to form centrosymmetric dimers is also present in these thioureas. Here we report structural and spectroscopic studies of five N-(2-pyridylethyl)-N'-arylthioureas in which the NH, rather than the N'H in the previously studied thioureas [2–4], is capable of intramolecular hydrogen bonding to the pyridyl nitrogen. N'H is expected to be involved in intermolecular hydrogen bonding to a sulfur of a neighboring molecule. The five thioureas studied here and their symbols are

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Fig. 1. Preparation reaction for the 5-thiourea prepared from 2-amionethylpyridine.

the following: N-(2-pyridylethyl)-N'-phenylthiourea, PyEtTuPh; N-(2-pyridylethyl)-N'-p-tolylthiourea, PyEtTupT; N-(2-pyridylethyl)-N'-p-bromophenylthiourea, PyEtTupBrPh; N-(2-pyridylethyl)-N'-pnitrophenylthiourea, PyEtTupNO<sub>2</sub>Ph and N-(2-pyridylethyl)-N'-p-methoxyphenylthiourea, PyEtTupO-MePh.

## 2. Experimental

The various isothiocyanates and 2-aminoethylpyridine were purchased from Aldrich and used as received. The desired aryl isothiocyanate was mixed in a 1:1 molar ratio with 2-aminoethylpyridine in anhydrous EtOH, and the resulting mixture gently refluxed for a minimum of 1 h. On cooling and slowly evaporating the reactant mixture (35°C), the thioureas crystallized from solution (see Fig. 1). The solids were filtered, washed with cold isopropanol followed by anhydrous ether, dried on a warm plate and then stored until required for characterization. Their melting points are as follows: PyEtTuPh, 112-114°C; PyEtTupT, 109-111°C; PyEtTupBrPh, 128-130°C; PyEtTupNO<sub>2</sub>Ph, 159–160°C; and PyEtTupO-MePh, 119-120°C. Their <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> with a Varian Gemini 2000 300 MHz spectrometer. IR spectra were recorded as Nujol mulls between NaCl plates with a Nicolet 5SCX FT Spectrometer and UV spectra with a Cary 5E spectrophotometer in 1 cm cells.

Crystals of the thioureas were grown by slow evaporation of anhydrous ethanolic solutions (filtrates) at room temperature. The crystals were mounted in random orientation on a glass fiber on a Siemens P4 Four Circle Diffractometer or a Nonius Mach 3 diffractometer. The structures were solved with direct methods and missing atoms were found by difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic temperature factors and all hydrogens were found on the difference-Fourier map. The H atoms of CH were allowed to ride on the C atoms and assigned a fixed isotropic temperature factor,  $U = 0.05 \text{ Å}^2$ . Only the coordinates of the H atoms attached to N and N' were refined. Scattering factors for PyEtTuPh and PyEtTupOMePh were taken from International Tables for X-ray Crystallography (1974, Vol. IV), and all calculations were done with the SHELXTL PC<sup>™</sup> program package [5]. Scattering factors for PyEtTupT, PyEtTupBrPh and PyEtTup-NO<sub>2</sub>Ph are from Wassmaire and Kirfel [6], and calculations were done by maXus, version 2.0 [7].

The crystallographic data and methods of data collection, solution and refinement are shown in Tables 1 and 2; the atomic coordinates and equivalent isotropic displacement coefficients are included in the deposited material (CCDC), as are a complete list of bond distances and angles. The CCDC#s are as follows: PyEtTuPh = 113 878, PyEtTupT = 113 877, PyEtTupBrPh = 113 879, PyEtTupNO<sub>2</sub>Ph = 113 881 and PyEtTupOMePh = 113 880.

# 3. Results and discussion

# 3.1. Structural studies

PyEtTupBrPh, PyEtTupNO<sub>2</sub>Ph and PyEtTupOMePh

Table 1									
Crystallographic data	and methods	of data collection	, solution and	refinement	for Py	yEtTuPh	and P	<b>y</b> EtTuj	ьT

Crystal data	PyEtTuPh	PyEtTupT
Empirical formula	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> S	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> S
Crystal color, habit	Colorless prism	Yellow, prism
Crystal size (mm)	$0.40 \times 0.24 \times 0.12$	$0.30 \times 0.26 \times 0.12$
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	8.616(1)	8.804(2)
b (Å)	9.663(1)	9.951(2)
c (Å)	9.761(1)	10.255(2)
$\alpha$ (°)	102.05(1)	115.03(2)
$\beta$ ((°)	102.36(1)	105.93(2)
$\gamma$ (°)	116.17(1)	104.04(2)
Volume ( $Å^3$ )	668.5(1)	713.43(1)
Z	2	2
Formula weight	257 35	271.4
Density (calc.) $(g/cm^3)$	1 279	1 30
Absorp Coeff $mm^{-1}$	2 022	2 173
F(000)	272	288
Data collection	_/_	200
Diffractometer	Siemens P4/PC	Nonius Mach 3
Radiation $\lambda$ (Å)	$C_{\rm U} K \alpha (1.54178 \text{ Å})$	$M_0 K_\alpha(0.70930 \text{ Å})$
Temperature (K)	293(2)	293(2)
Monochromator	Highly oriented	2,5(2)
Graphite crystal	Highly oriented	
Graphite crystal	inginy oriented	
2A range	$3 \text{ to } 110.0^{\circ}$	$2 \text{ to } 55 0^{\circ}$
Scan type	a/2 A	ω/θ
Scan range (a)	0.70°	0.80°
Index ranges	$-1 \le h \le 0$	0.60
index ranges	1 = 1 = 9 -0 < k < 0	0 = 1 = 11 -12 < k < 12
	-10 < 1 < 10	12 = K = 12 -13 < 1 < 12
Paflactions collected	2053	3580
Ind Reflec $(R_{\rm o})$	1647(5.62%)	3249(1.70%)
Observed reflections	1047 (3.02%) 1282 (I > 2.0 $\sigma$ (I))	3249(1.70%) 2612 (I $> 2.0 \times (1)$ )
Absorption correction	$1382 \{1 \ge 2.00(1)\}$	$2012 \{1 > 3.00(1)\}$
Solution and refinament	Senn-empirical	ψ-scan
Solution and replacement	Direct methods	Direct methods
Solution method Coodmass of fit on $E^2$	1 085	
Data /restraints/normators	1.083	2.404
Data /restraints/parameters	1047/27170	2012/0/178
Largest diff. Peak (eA )	0.294	0.07
Largest dill. noie (eA )	-0.755	-0.51
Largest and mean $\Delta/s$	0.000, 0.000	0.000, 0.000
K1, WKZ	0.0093, 0.1935	$0.0300, 0.0022 (\omega K)$
$\kappa_1, w\kappa_2$ (all data)	0.0799, 0.2085	$U.U/U05, U.U05/(\omega K)$
Programs used	SHELXTL PLUS	Maxus

 $^{\rm a}$  The 2 N–H bond distances were restrained to 0.90(1) Å.

are in a conformation resulting from intramolecular hydrogen bonding of NH to the pyridine nitrogen, N1. However, for PyEtTuPh and PyEtTupT, the NH hydrogen is further from the pyridyl nitrogen than an NH hydrogen from a neighboring molecule. Perspective views of PyEtTupT, representing of N-(2)-pyridylethyl-N'-arylthioureas without intramolecular hydrogen bonding, and PyEtTupNO<sub>2</sub>Ph,

#### Table 2

Crystallographic data and methods of data collection,	solution and refinement for	PyEtTupBrPh,	PyEtTupNO <sub>2</sub> Ph and	l PyEtTupMeOPh
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Crystal data	PyEtTupBrPh	PyEtTupNO <sub>2</sub> Ph	PyEtTupOMePh
Empirical formula	C <sub>14</sub> H <sub>14</sub> BrN <sub>3</sub> S	$C_{14}H_{14}N_4O_2S$	C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> OS
Crystal color, habit	Colorless prism	Yellow prism	Colorless, prism
Crystal size (mm)	$0.32 \times 0.24 \times 0.10$	$0.34 \times 0.24 \times 0.10$	$0.32 \times 0.28 \times 0.12$
Crystal system	Triclinic	triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/n$
a (Å)	9.536(1)	8.046(2)	11.526(2)
b (Å)	9.809(1)	8.602(3)	9.723(2)
<i>c</i> (Å)	10.042(2)	10.938(3)	13.460(2)
$\alpha$ (°)	115.88(1)	80.74(3)	90.00
β ((°)	96.80(1)	89.77(2)	100.49(2)
γ (°)	110.44(1)	77.00(3)	90.00
Volume (Å <sup>3</sup> )	750.0(6)	727.6(6)	1483.3(2)
Z	2	2	4
Formula weight	336.3	302.4	287.4
Density (calcd.) (g/cm <sup>3</sup> )	1.30	1.30	1.287
Absorp. Coeff., $mm^{-1}$	28.734	2.325	1.929
F(000)	356	316	608
Data collection			
Diffractometer	Nonius Mach 3	Nonius Mach 3	Siemens P4/PC
Radiation $\lambda$ (Å)	MoKα(0.70930 Å)	MoKα(0.70930 Å)	CuKα(1.54178 Å)
Temperature (K)	293(2)	293(2)	293(2)
Monochromator	Highly oriented Graphite crystal	Highly oriented graphite crystal	Highly oriented Graphite crystal
$2\theta$ range	2.0 to 55.0°	2.0 to 55.0°	3 to 110.0°
Scan type	$\omega/ heta$	$\omega/ heta$	$\theta/2\theta$
Scan range $(\omega)$	0.80	$0.80^{\circ}$	$0.80^{\circ}$
Index ranges	$0 \le h \le 12$	$0 \le h \le 10$	$-1 \le h \le 12$
-	$-11 \le k \le 11$	$-11 \le k \le 11$	$-1 \le k \le 10$
	$-13 \le 1 \le 12$	$-14 \le l \le 14$	$-14 \le l \le 14$
Reflections collected	3779	3722	2497
Ind. Reflec. $(R_{int})$	3644 (1.0 %)	3346 (3.3 %)	1859 (4.90 %)
Observed reflections	2346 {F > 3.0 $\sigma$ (I)}	2408 {F > 3.0 $\sigma$ (I)}	1655 {F > 3.0 $\sigma((F)$ }
Absorption correction	$\psi$ -scan	$\psi$ -scan	Face-indexed numerical
Solution and refinement			
Solution method	Direct methods	Direct methods	Direct methods
Goodness-of-fit on F2	0.833	1.293	1.28
Data/restraints/parameters	2346/0/172	2408/0/190	1859/0/221
Largest diff. peak ( $eÅ^{-3}$ )	0.294	0.52	0.19
Largest diff. hole $(eÅ^{-3})$	- 0.755	-0.27	-0.18
Largest and mean $\Delta/s$	0.000, 0.000	0.000, 0.000	0.029, 0.005
<i>R</i> 1, <i>wR</i> [ $I > 3\sigma(I)$ ]	0.0513, 0.0440	0.0407, 0.0343	0.0417, 0.0573 wR2
R1, $wR2$ (all data)	0.0918, 0.0499	0.0648, 0.0379	0.0459, 0.0602 wR2
Programs used	MaXus	MaXus	SHELXTL PLUS

representing those with intramolecular hydrogen bonding are shown in Figs. 2 and 3. Representative packing diagrams of PyEtTuPh and PyEtTupMeOPh are shown in Figs. 4 and 5. Inspection of Table 3 shows that the bond distances and angles for the five 2-pyridyl thioureas are within three orders of magnitude of their estimated standard deviations, and the largest differences occur close to the aryl substituent as would be expected. However, the nature of the aryl ring substituents does not have a large effect on the bond distances and angles of the thiourea moiety.

The intramolecular and intermolecular hydrogen bonding data are shown in Table 4. PyEtTupBrPh, PyEtTupNO<sub>2</sub>Ph, and PyEtTupMeOPh show similar



Fig. 2. A perspective view of PyEtTupT showing intermolecular hydrogen bonding.

distances and angles for their intramolecular N2-H2…N1 hydrogen bonds. Intramolecular N2…N1 distances and N2-H2...N1 angles for PyEtTuPh  $\{3.294(7) \text{ Å}, 124(3)^{\circ}\}$  and PyEtTupT  $\{3.352(2) \text{ Å}, 124(3)^{\circ}\}$  $110(11)^{\circ}$  are well outside the range normally associated with N-H···N hydrogen bonding (2.6-3.1 Å, 130-180°) [8]. Instead, these molecules have intermolecular N2-H2···N1A hydrogen bonds. All five thioureas are involved in intramolecular N3-H···SA hydrogen bonding and the non-bonding distance between N3 and a SA on a neighboring molecule is in the normal range of 3.2–3.5 Å [9]. Two molecules arrange themselves, so that both N3H's hydrogen bond with the other sulfur, to form dimers with eight-members. The N2-H···SA angles for these five thioureas are quite similar. Neither the nitro group of PyEtTupNO<sub>2</sub>Ph nor the methoxy group of PyEtTupMeOPh are involved in intermolecular hydrogen bonding (i.e. classical hydrogen bonding).

Table 5 shows the angles between the mean planes for the pyridyl ring, the thiourea moiety, and the aromatic ring as well as the mean plane deviations for the three. The thiourea moiety has an average deviation from the mean plane of no greater than 0.003 Å for any of these thioureas and C9 is the atom that has the greatest deviation from the mean plane, except in PyEtTupT where N2 shows the greatest deviation. Since PyEtTuPh and PyEtTupT do not intramolecularly hydrogen bond and PyEtTupBrPh, PyEtTupNO<sub>2</sub>Ph and PyEtTupMeOPh do, there is a significant difference in the angles between the pyridyl ring and thiourea moiety. This angle is greater in the molecules with intermolecular N2– $H2\cdots$ N1A hydrogen bonds (i.e. PyEtTuPh and PyEtTupT), suggesting that the pyridyl ring is rotated to point to N2H hydrogen of another molecule.

#### 3.2. Spectral studies

The u.v. spectra (DMF) show two bands for four of the *N*-(2-pyridylethyl)-*N*'-arylthioureas and a three bands for PyEtTupNO<sub>2</sub>Ph. The higher energy band, ca. 37,500 cm<sup>-1</sup> we assign to a combination of  $\pi \rightarrow \pi^*$  transitions from both the pyridinyl and aromatic



Fig. 3. A perspective view of PyEtTupNO<sub>2</sub>Ph.



Fig. 4. Packing diagram for PyEtTuPh.



Fig. 5. Packing diagram for PyEtTupOMePh.

rings. The band in the 34 500 cm<sup>-1</sup> region of the spectrum with a molar absorptivity of approximately  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$  is due to a combination of  $n \rightarrow \pi^*$  bands of the heterocyclic ring and thiourea moiety. PyEtTupNO<sub>2</sub>Ph has a band at 28,120 cm<sup>-1</sup> due to a  $n \rightarrow \pi^*$ transition of the nitro group which also has a molar absorptivity of about  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . The

presence of the nitro group shifts the other two bands to higher energy compared to their positions in the other four thioureas.

In the infrared spectra of the five thioureas we have assigned  $\nu(N'H)$  to medium intensity absorptions in the 3260–3325 cm<sup>-1</sup> region. The thioamide IV band, which owes considerable intensity to  $\nu(CS)$ , is assigned in the range 800–860 cm<sup>-1</sup> agreement with previously studied thioureas [3,4].

In contrast to their crystal structures, the chemical shifts for N2H do not indicate intramolecular hydrogen bonding in CDCl<sub>3</sub> solution for PyEt-TupBrPh, PyEtTupNO<sub>2</sub>Ph and PyEtTupMeOPh. The fact that these five thioureas have N2-H2...SA angles that are at the low end of the range (i.e.  $120-130^{\circ}$ ) for this type of hydrogen bond is probably related to its disappearance on dissolution in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectra show some variation in the shift of the resonance due to the aryl substituent with the resonances for both NHs being affected (Table 6). The increased negative inductive effect of the nitro group causes a downfield shift while the methoxy function causes an upfield shift; the  $\delta$  values vary in the order NO<sub>2</sub> > Br > H > Me > OMe for the resonance we have assigned to N'H, which is our basis for the assignment. All other chemical shifts shown in Table 6 are affected to a lesser extent by the aryl substituents.

In conclusion, the lack of intramolecular hydrogen

Table 3

Selected bond distances (Å) and angles (°) for PyEtTuPh, PyEtTupT, PyEtTupBrPh, PyEtTupNO2Ph and PyEtTupOMePh

	PyEtTuPh	PyEtTupT	PyEtTupBrPh	PyEtTupNO <sub>2</sub> Ph	PyEtTupOMePh
Bond distances (Å	)				
S1-C9	1.688(4)	1.698(1)	1.686(6)	1.693(1)	1.691(2)
N1-C2	1.331(6)	1.336(2)	1.345(8)	1.340(2)	1.332(4)
N1-C6	1.332(7)	1.349(2)	1.349(8)	1.341(2)	1.345(4)
N2-C8	1.444(6)	1.449(2)	1.464(7)	1.463(1)	1.454(4)
N2-C9	1.326(6)	1.325(2)	1.336(6)	1.331(1)	1.324(4)
N3-C9	1.358(6)	1.372(2)	1.366(7)	1.366(1)	1.354(4)
N3-C10	1.418(6)	1.432(2)	1.421(7)	1.417(1)	1.432(3)
Bond angles (°)					
C2-N1-C6	117.1(4)	116.3(2)	117.1(5)	118.0(1)	117.6(3)
N1-C2-C7	116.8(4)	115.4(1)116.2(8)	116.0(2)	117.3(3)	
C7-C8-N2	111.1(4)	108.8(1)	111.8(8)	111.3(3)	113.1(3)
C8-N2-C9	123.6(4)	123.0(1)	122.8(4)	123.3(1)	126.1(2)
N2-C9-S1	122.6(3)	123.6(1)	122.8(4)	123.2(1)	123.5(2)
N2-C9-N3	117.4(4)	117.7(1)	117.6(4)	117.9(1)	117.2(2)
N3-C9-S1	120.1(4)	118.6(1)	119.6(4)	118.8(1)	119.3(2)
C9-N3-C10	128.1(4)	127.1(1)	127.8(4)	128.3(1)	127.6(2)

Mode	PyEtTuPh	PyEtTupT	PyEtTupBrPh	PyEtTupNO <sub>2</sub> Ph	PyEtTupOMePh
Intramolecular			2 26(1)	2 162(2)	2 28(2)
$n_2 \cdots n_1 (A)$ $n_2 - h_2 \cdots n_1 (A)$			2.20(1) 2.94(2)	2.102(3) 2 900(4)	2.38(3) 2.841(3)
$\angle N2-H2\cdots N1$ (°)			128(5)	130(2)	115(3)
Intermolecular					
H2…N1A (Å)	2.39(3)	2.19(1)			
N2−H2…N1A (Å)	$3.040(7)^{a}$	$2.996(1)^{b}$			
∠N2–H2…N1A (°)	130(3)	156(13)			
H3···SA (Å)	2.51(2)	2.51(1)	2.536(2)	2.44(7)	2.57(4)
N3−H3···SA (Å)	$3.382(4)^{c}$	$3.460(1)^{d}$	3.375(6) <sup>b</sup>	$3.423(2)^{e}$	$3.394(3)^{d}$
∠N3–H3…SA (°)	165(4)	161(11)	162(5)	165(2)	165(3)

Intramolecular and intermolecular	hydrogen bond	l distances (Å)	and angles (°)
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 $x^{a} - x + 1, -y, -z + 2.$ 

 $^{b}-x+1, -y+1, -z+1.$ 

c -x, -y, -z + 1. d -x + 2, -y + 2, -z.

 $e^{-x}$ , -y + 1, -z + 1.

Table	5
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Thiourea mean plane deviation and angles between planes (plane A = mean plane of pyridine ring, plane B = mean plane of the thiourea moiety, N-C(S) - N' and plane C = mean plane of the six carbons of the aromatic ring)

Compound	А	В	С	$\angle A/B$	∠B/C	∠A/C
PyEtTuPh	0.0082(3)	0.0023(2)	0.0028(2)	74(1)	49(1)	28(1)
PyEtTupT	0.0041(2)	0.0010(3)	0.0049(2)	80(4)	48(4)	40(4)
PyEtTupBrPh	0.0065(6)	0.0001(1)	0.0056(4)	51(4)	55(3)	23(4)
PyEtTupNO <sub>2</sub> Ph	0.0038(3)	0.0027(2)	0.0065(3)	36(4)	50(4)	21(4)
PyEtTupOMePh	0.0066(3)	0.0020(3)	0.0052(3)	40(1)	55(1)	16(1)

Table 6

<sup>1</sup>H NMR (δ), ultraviolet (cm<sup>-1</sup>) and infrared (cm<sup>-1</sup>) spectral data for PyEtTuPh, PyEtTupT, PyEtTupBrPh, PyEtTupNO<sub>2</sub>Ph and PyEtTupO-MePh

Compound	C6H	N'H	NH	$CH_2N$	CCH <sub>2</sub>	$\pi \to \pi^*$	$n \to \pi^*$	$\nu$ (C=S)	$\nu(N'H)$
PyEtTuPh	8.145	8.067	7.939	4.020	3.029	37,630	34,760(4.92) <sup>a</sup>	836m	3296sh
PyEtTupT	8.172	7.730	7.660	4.026	3.042	37,580	34,830(4.95)	836m	3263m
PyEtTupBrPh	8.212	8.212	7.899	4.078	3.096	37,880	33,930(5.00)	826m	3280m
PyEtTupNO <sub>2</sub> Ph	8.295	8.886	8.572	4.144	3.170	39,560	35,300(5.02) 28,180(5.06)	858m	3313m
PyEtTupOMePh	8.144	7.625	7.594	4.003	3.016	37,580	34,590(4.97)	820m	3322m

<sup>a</sup> Values in parentheses are log  $_{10}\epsilon$ .

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Table 4

bonding with the pyridyl nitrogen for PyTuEtPh and PyTuEtpT, which have the smallest para substituents on their aromatic rings (i.e. H and Me, respectively) is somewhat surprising. As indicated earlier this results in the pyridyl mean plane being at a much larger angle (i.e.  $74-80^{\circ}$ ) with the thiourea moiety mean plane than found for the other three thioureas (i.e. 36-51°). The behavior of these latter thioureas in not due to an inductive effect of the aryl substituent since both PyEtTupNO<sub>2</sub>Ph and PyEtTupMeOPh do form intramolecular hydrogen bond, but may be a steric effect since their aryl substituents are larger. The intermolecular hydrogen bond involving the pyridyl nitrogen in PyTuEtPh and PyTuEtpT results in a slightly longer N2-H1…N1A than found for the intramolecular hydrogen bonding. We are continuing to study additional PyEtTu aromatic derivatives with other para substituents, as well as meta and ortho substituents.

Supplementary material: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1003/m. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, teched@chemcrys.cam.ac.uk.

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