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Structural and spectral studies of N-(2-pyridyl)-N'-tolylthioureas

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Dedicated with best wishes to Professor Gottfried Heinisch on the occasion of his 60th birthday

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Abstract

N-(2-pyridyl)-N'-o-tolylthiourea, monoclinic, P2₁/c, a = 5.127(1), b = 19.854(2), c = 12.077(2) Å, $\beta = 94.96(1)^{\circ}$, V = 1224.7(2) Å³, Z = 4, $\mu = 2.177 \text{ mm}^{-1}$, N-(2-pyridyl)-N'-m-tolylthiourea, triclinic, P - 1, a = 9.811(2), b = 9.887(4), c = 13.595(3) Å, $\alpha = 74.91(3)$, $\beta = 83.58(2)$, $\gamma = 76.27(2)^{\circ}$, V = 1235.(7) Å, Z = 4, $m = 2.469 \text{ mm}^{-1}$ and N-(2-pyridyl)-N'-p-tolylthiourea, triclinic, P - 1, a = 9.935(2), b = 11.488(2), c = 12.569(2) Å, $\alpha = 63.91(2)$, $\beta = 88.60(2)$, $\gamma = 75.04(2)^{\circ}$, V = 1238.1(2) Å³, Z = 4, $\mu = 2.154 \text{ mm}^{-1}$ all have an intramolecular hydrogen bond between N'H and the pyridyl nitrogen, as well as intermolecular hydrogen bonding between NH and a thione sulfur of a second molecule to form centrosymmetric dimers. Solution ¹H NMR studies (CDCI₃) show the N'H resonance considerably downfield for each thiourea and its position, as well as that of NH, are affected by substituents on the phenyl ring. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heterocyclic thioureas; Hydrogen bonding; Crystal structure

1. Introduction

Although ¹H NMR has correctly predicted intramolecular hydrogen bonding between the pyridyl nitrogen and N'H [1], only recently has a structural study been reported concerning N-(2-pyridyl)-N'phenylthiourea [2]. Studies of a number of Nbenzoyl-N'-thioureas have shown them to be in the thioamidic form and to possess an intramolecular hydrogen bond between N'H and the benzoyl oxygen [3–8]. There is also a weak intermolecular N2H hydrogen bond with a sulfur of a neighboring molecule to form a two-dimensional network in these latter thioureas. In addition, there are reports of crystal

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structures of substituted thioureas lacking intramolecular hydrogen bonding, but studying the intermolecular hydrogen bonding between an N–H and a sulfur in a neighboring molecule [9–13]. A more recent study of substituted N-(2-pyridyl)-N'-phenylthioureas involves methyl substituents on the pyridyl ring (i.e., picolyl and lutidyl derivatives) [14]. Here we report the crystal structures and lattice arrangements for thioureas having methyl groups situated on the aromatic ring (i.e., tolyl derivatives), Fig. 1, which possess both intramolecular and intermolecular hydrogen bonding.

2. Experimental

2-aminopyridine was purchased from Aldrich and

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Fig. 1. A representation of a N-(2-pyridyl)-N'-tolylthiourea showing expected intra-and intermolecular bonding.

used as received. It was mixed in a 1:1 molar ratio with o-tolyl-, m-tolyl-, or p-tolylisothiocyanate (Aldrich) in anhydrous ethanol, and the resulting mixture gently refluxed for a minimum of 1 h. On cooling and slowly evaporating (35°C) the reactant mixture, the thioureas crystallized from solution. They were filtered, washed with cold isopropanol followed by anhydrous ether, dried on a warm plate and then stored until required for characterization. The yields are ca. 65% for each of the thioureas and the melting points are as follows: PyTuoT, 183°-185°; PyTumT, 167°-169°; and PyTupT, 183°-185°. The NMR spectra were recorded in d⁶-DMSO with a Varian Gemini 2000 300 MHz spectrometer. Infrared and ultraviolet spectra were recorded with Perkin-Elmer 783 and Hewlett Packard 8452 A Diode Array spectrophotometers, respectively.

Colorless, prismatic crystals of the thioureas were grown by slow evaporation of anhydrous ethanolic solutions (filtrates) at room temperature. 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 fixed isotroic temperature factor, $U = 0.06 \text{ Å}^2$. Only the coordinates of the H atoms attached to N and N' were refined. Refinement of the structures was made by full-matrix least-squares. Scattering factors for N-(2-pyridyl)-N'-o-tolylthiourea, PyTuoT, and N-(2pyridyl)-N'-p-tolylthiourea, PyTupT, were taken from International Tables for X-ray Crystallography (1974, Vol. IV), and all calculations were done with the SHELXTL PCTM program package [15]. Scattering factors for N-(2-pyridyl)-N'-m-tolylthiourea, PyTumT, are from Wassmaire and Kirfel [16], and calculations were done by maXus, version 2.0 [17].

3. Results and discussion

3.1. Structural studies

The crystallographic data and methods of data collection, solution and refinement for PyTuoT, PyTumT and PyTupT are shown in Table 1 and 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: PyTuoT = 102612,PyTumT = 102611and PyTupT = 102613.

The molecular structures of the three thioureas are shown in Figs. 2–4.,, All three are in a conformation resulting from intramolecular hydrogen bonding of the N'H to the pyridine nitrogen, N1, in a manner similar to the benzoyl thioureas and "trans–cis" like N-cyclohexyl-N'-phenylthiourea [12]. Inspection of Table 2 shows that the bond distances and bond angles for the three 2-pyridyl thiureas are within three orders of magnitude of the estimated standard deviations. Thus, the position (i.e., ortho, meta or para) of the methyl group on the aryl ring has no significant effect on the bond distances and angles of the thiourea moiety.

Table 3 shows bond distances and angles for PyTuoT, PyTumT and PyTupT along with other thioureas having a functional group able to accommodate a similar intramolecular hydrogen bond, as well as representative N,N'-substituted thioureas that do not have intramolecular hydrogen bonding [9-13]. The only significant differences between the pyridyl thioureas and the previously studied intramoleculary hydrogen bonded thioureas is that the pyridyl thioureas have shorter N-C7 bonds and their C7-S1 bond is marginally longer. There is essentially no difference in the N'-C7 bonds as would be expected as both groups of thioureas have aromatic rings attached to N'. The pyridyl thioureas do not have the electron withdrawing carbonyl group attached to N, which apparently allows the N-C7 bond to have

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Crystallographic	data and method	is of data coll	lection solution	and refinement for	PyTuoT and PyTunT
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Crystal Data	РуТиоТ	PyTumT	РуТирТ
Empirical Formula	$C_{13}H_{13}N_3S$	C ₁₃ H ₁₃ N ₃ S	C ₁₃ H ₁₃ N ₃ S
Crystal Color, Habit	Colorless, prism	Colorless, prism	Colorless, prism
Crystal Size (mm)	$0.32 \times 0.28 \times 0.20$	$0.30 \times 0.26 \times 0.18$	$0.40 \times 0.14 \times 0.12$
Crystal System	Monoclinic	Triclinic	Triclinic
Space Group	$P2_1/c$	P - 1	P - 1
<i>a</i> , Å	5.127(1)	9.811(2)	9.935(2)
b, Å	19.854(2)	9.887(4)	11.488(2)
<i>c</i> , Å	12.077(2)	13.595(3)	12.569(2)
α , °	90(0)	74.91(3)	63.91(2)
$\beta,^{\circ}$	94.96(1)	83.58(2)	88.60(2)
$\lambda,^{\circ}$	90(0)	76.27(2)	75.04(2)
Volume, Å ³	1224.7(2)	1235.2(7)	1238.1(2)
Ζ	4	4	4
Formula weight	243.3	243.3	243.3
Density (calcd.), g/cm ³	1.320	1.30	1.305
Absorp. coeff., mm^{-1}	2.177	2.469	2.154
F(000)	512	512	512
Data Collection			
Diffractometer	Siemens P4/PC	Nonius Mach 3	Siemens P4/F
Radiation, (wavelength)	CuKα, (1.54178 Å)	MoKα, (0.70930 Å)	CuKα, (1.54178 Å)
Temperature (K)	293	293	293
Monochrometer	Highly oriented graphite crystal	Highly oriented graphite crystal	Highly oriented graphite crystal
2θ range	3.0°-110.0°	2.0°-55.0°	3.0°-110.0°
Scan type	$\theta/20$	$\omega/ heta$	$\theta/2\theta$
Scan range (ω)	0.70°	0.80°	0.84°
Index ranges	$0 \le h \le 5$	$0 \le h \le 12$	$0 \le h \le 5$
	$0 \le k \le 21$	$-12 \le k \le 12$	$0 \le h \le 21$
	$-12 \le l \le 12$	$-17 \le l \le 17$	$-13 \le l \le 12$
Reflections collected	1641	6280	3349
Ind. reflec. (R_{int})	1440 (2.7 %)	5654 (2.56 %)	3133 (2.56 %)
Observed reflections	1299 { $F > 4.0\sigma(F)$ }	2672 $\{l > 3.0\sigma(l)\}$	2672 { $F > 3.0\sigma(F)$ }
	Face-indexed		Face-indexed
Absorption correction	Numerical	Ψ-scan	Numerical
Max. and min. transmissions	0.8232 and 0.6625	0.999 and 0.929	0.7496 and 0.5428
Solution and refinement			
Solution method	Direct methods	Direct methods	Direct methods
Goodness-of-Fit	1.34	2.741	1.30
Data/parameter ratio	8.1:1	12.6 : 1	8.4 : 1
Largest diff. Peak eÅ ⁻³	0.30	0.38	0.26
Largest diff. Hole eÅ ⁻³	-0.36	-0.34	-0.33
Largest and Mean D/s	0.000, 0.000	0.000, 0.000	0.000, 0.000
R	0.0442	0.0580	0.0489
ωR	0.0677	0.0650	0.0712
Programs used	SHELXTL PLUS	maXus	SHELXTL PLUS

slightly more double bond character. Also, there is no significant difference in the thiourea moiety's bond angles between the present thioureas and those previously studied with intramolecular hydrogen bonding [3–7]. In general, the three thioureas included in Table 3 having only intramolecular

hydrogen bonding [9,11,12] show the following differences from thioureas with intermolecular hydrogen bonding: the N–C7 bond is shorter, N–C7–S1 angle larger and the N'–C7–S1 angle smaller.

The intramolecular hydrogen bonding common to all three of the present thioureas shows somewhat



Fig. 2. A perspective view of PyTuoT showing intramolecular hydrogen bonding.

different N'H...N non-bonding distances which appear to be related to the weak electronic effect of the methyl group in the ortho and para positions. PyTumT has the longest N'H...N distance(s) of 2.697(2), 2.697(2) Å followed by PyTuoT with distance(s) of 2.687(4) Å. The shortest distance, 2.646(4),2.665(4) Å, for PyTupT indicates not only an electronic effect, but also a steric effect.



Fig. 3. A perspective view of PyTumT showing the two independent molecules of the unit cell.



Fig. 4. A perspective view of PyTupT showing both intramolecular and intermolecular hydrogen bonding.

As was found for N-benzoyl-N'-(4-methoxyphenyl) thiourea [8], NH is involved in intermolecular hydrogen bonding with a sulfur from a neighboring molecule. The previously studied N-substituted and N,N'-substituted thioureas average 3.46 Å [9–13], the smallest N...S distance being 3.363(1) Å for N-diethyl-N'-o-tolythiourea [11] and the largest 3.563(1) Å for N-cyclohexyl-N'-cyclohexylthiourea [10]. The present compounds, PyTuoT, PyTumT and PyTupT, have N...S non-bonding distances of 3.401(2) Å, 3.387 and 3.410(2) Å and 3.352 and 3.523(4) Å, respectively, which is close to the range found in previous studies [9–13]. The shorter nonbonding N...S distance for PyTupT suggests a

Table 2

Selected bond distances (Å) and angles (°) for	for PyTuoT, PyTumT and PyTupT.
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Bond distances (Å)	PyTuoT	PyTumT ^a		PyTupT ^a		
S1-C7	1.678(3)	1.684(2)	1.684(2)	1.684(4)	1.672(4)	
N1-C2	1.329(4)	1.332(3)	1.329(3)	1.326(6)	1.340(6)	
N1-C6	1.327(5)	1.352(3)	1.354(3)	1.345(5)	1.341(6)	
N2-C2	1.392(4)	1.407(3)	1.408(3)	1.397(5)	1.391(5)	
N2-C7	1.370(4)	1.377(3)	1.373(3)	1.373(4)	1.378(6)	
N3-C7	1.336(4)	1.331(3)	1.334(3)	1.324(6)	1.355(6)	
N3-C8	1.440(4)	1.447(3)	1.443(3)	1.435(4)	1.433(6)	
Bond angles (°)						
C2-N2-C7	130.0(4)	130.2(2)	130.4(2)	129.6(4)	130.7(6)	
C7-N3-C8	124.4(4)	124.2(2)	123.4(2)	128.0(3)	125.4(7)	
N1-C2-N2	119.7(4)	119.4(2)	119.0(2)	119.3(3)	119.2(6)	
N2-C2-C3	117.9(4)	117.6(2)	118.0(2)	118.3(4)	118.7(7)	
S1-C7-N2	119.7(4)	118.8(2)	118.4(2)	118.6(3)	119.0(6)	
S1-C7-N3	123.4(4)	123.5(2)	123.7(2)	125.4(2)	124.5(6)	
N2-C7-N3	116.9(4)	117.7(2)	117.9(2)	116.0(2)	116.4(7)	
N3-C8-C9	120.5(4)	119.7(2)	120.0(2)	118.6(3)	118.5(7)	
N3-C8-C13	117.8(4)	118.1(2)	118.5(2)	121.3(3)	121.9(7)	

^a The second column represents the analogous bonds in the second molecule.

Table 3

	Bond distan	Bond distances, Å			Bond angles, °		
Compound	N2-C7	S1-C7	N3-C7	N2-C7-N3	N2-C7-S1	N3-C7-S1	Ref
BzOTuPr ^a	1.393(5)	1,678(4)	1.332(7)	117.4(3)	118.5(3)	124.1(3)	[4]
(EtOH)2TuPhb	1.391(2)	1.672(2)	1.335(3)	114.3(2)	123.30(14)	122.35(14)	[5]
BzOTupNO ₂ Ph ^c	1.393(3)	1.658(2)	1.344(3)	115.0(2)	118.3(2)	126.6(2)	[6]
BzOTupMeOPh ^d	1.392(4)	1.659(3)	1.329(4)	115.4(3)	119.2(2)	125.4(2)	[7]
PhTuPh ^e	1.349(4)	1.681(5)	1.349(4)	113.9(4)	123.0(2)	123.0(2)	[9]
Me ₂ TuoT ^f	1.356(4)	1.693(3)	1.337(4)	115.6(3)	121.5(3)	122.9(2)	[11]
Et ₂ TuoT ^g	1.358(2)	1.702(2)	1.344(2)	115.63(14)	121.30(12)	123.07(12)	[11]
ChTuPh ^h	1.332(2)	1.696(2)	1.347(2)	117.33(15)	123.62(12)	119.05(13)	[12]
PyTuPh ⁱ	1.374(4)	1.682(3)	1.335(4)	116.8(5)	118.6(4)	124.6(4)	[2]
6MePyTuPh ^j	1.375(4)	1.679(3)	1.333(4)	115.8(5)	117.3(4)	126.9(4)	[14]
4,6MePyTuPh ^k	1.366(4)	1.689(3)	1.341(4)	115.5(2)	117.6(2)	126.9(2)	[14]
PyTuoT	1.370(4)	1.678(3)	1.336(4)	116.9(4)	119.7(4)	123.4(4)	1
PyTumT	1.377(3)	1.684(2)	1.331(3)	116.7(2)	118.8(2)	123.5(2)	1
•	1.373(3)	1.684(2)	1.334(3)	117.9(2)	118.4(2)	123.7(2)	1
PyTupT	1.373(4)	1.684(4)	1.324(6)	116.0(3)	118.6(3)	125.4(2)	1
•	1.378(6)	1.672(4)	1.354(6)	116.4(7)	119.0(6)	124.5(6)	

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

^a N-benzoyl-N'-propylthiourea

^b N,N-di(hydroxyethyl)-N'-phenylthiourea

^c N-benzoyl-N'-(4-nitrophenyl) thiourea

^d N-benzoyl-N'-(4-methoxyphenyl)thiourea

f N-dimethyl-N'-o-tolythiourea

^g N-diethyl-N'-o-tolythiourea

h N-cyclohexyl-N'-phenylthiourea

ⁱ N-(2-pyridyl)-N'-phenylthiourea

^j N-6-methy-2-pyridyl-N'-phenylthiourea

^k N-4,6-dimethy-2-pyridyl-N'-phenylthiourea

lower steric effect by the methyl group than for PyTuoT and PyTumT. The intermolecular N–H...S bond angles for PyTuoT, PyTumT and PyTupT are $159(2)^{\circ}$, 161 and $162(2)^{\circ}$ and 167 and $171(4)^{\circ}$, which fall in the range of $140(3)^{\circ}$ (N-dimethyl-N'-otolylthiourea) [11] and $170(1)^{\circ}$ (N-ethyl-N'ethylthiourea) [9] found in previous structural studies of substituted thioureas. In addition to the N–H...S hydrogen bond, the sulfur is also interacting with a pyridyl hydrogen, C3H, with a C–H...S nonbonding distance of 3.619(3) Å, 3.564 and 3.635(2) Å and 3.528 and 3.801(5) Å and non-bonding angle of $138.5(3)^{\circ}$, 144 and 141.2(2)° and 145.6% and 146.7° for PyTuoT, PyTumT and PyTupT, respectively.

For PyTuoT, PyTumT and PyTupT the various torsion angles involving the thiourea moiety (e.g., C7-N2-C2-C3, C8-N3-C7-S1 etc.) are not very different from 0° or 180°. Thus, these molecules are

rather planar with the N1–C2–N2–C7–N3 plane deviating to the greatest extent in the three molecules; the mean plane deviations for PyTuoT, PyTumT and PyTupT are 0.0594 Å, 0.0141 Å and 0.0348 Å, respectively.

The angles between planes also give information about the molecules with the dihedral angle between the pyridyl and aryl planes being $67.4(1)^\circ$; 80.2(1), $78.59(6)^\circ$ and $58.8(1)^\circ$, $58.6(1)^\circ$ for PyTuoT, PyTumT and PyTupT, respectively, which are considerably greater than the $11.24(7)^\circ$ and $13.89(9)^\circ$ found for previously studied picolyl and lutidyl thioureas, 6MePyTuPh and 4, 6MePyTuPh [14], respectively, but in the range of $63.2(1)^\circ$ found for unsubstituted N-(2-pyridyl)-N'-phenylthiourea, PyTuPh [2]. The pyridyl ring has an angle with the thiourea moiety plane, N2–N3–C7–S1, of $13.6(2)^\circ$, $4.6(1)^\circ$, $2.08(4)^\circ$ and $10.2(1)^\circ$, $2.1(1)^\circ$ for PyTuoT, PyTumT and

^e N, N'-diphenylthiourea

¹This work.

ν (C=S)	$\nu(\text{NH})$	Ref.
857 m	3195 m	[14]
850 M	3197 m	[14]
828 m	3205 m	[14]
850 m	3200 m	e
831 m	3185 m	e
818m	3200m	e
	831 m 818m	831 m 3185 m 818m 3200m

¹H, ¹³C NMR (δ), ultraviolet and infrared spectral date for PyTuoT, PyTumT and PyTupT.

^a log ϵ

Table 4

^b N-2-pyridyl-N'-phenylthiourea

^c N-6-methy-2-pyridyl-N'-phenylthiourea

^d N-4, 6-dimethy-2-pyridyl-N'-phenylthiourea

^e This work.

PyTupT compared to $3.89(3)^{\circ}$, $4.66(3)^{\circ}$ and $5.4(1)^{\circ}$ for 6MeTuPh, 4,6MeTuPh, andPyTuPh, respectively. The phenyl ring has angles with the thiourea moiety of 75.5(1)°, 76.1(1)°, 77.2(1)° and 55.5(1)°, 56.5(1)° for PyTuoT, PyTumT and PyTupT respectively, compared to 11.17(8)°, 13.23(6)° and 58.0(1)° for 6MeTuPh, 4,6MeTuPh, and PyTuPh. Therefore, based on these six thioureas, it appears that substitution on the pyridyl ring makes the molecule more planar, but ortho substitution on the aryl ring makes the thiourea less planar. The general order of the planarity these decreasing of thioureas is 6MePyTuPh > 4,6MePyTuPh > PyTupT >PyTuPh > PyTuouT > PyTumT. Further, PyTumT has the longest non-bonding N-H...N distance $\{2.697 (2) \text{ Å}\}$ and the others fall in the 2.64 Å except for 4,6MePyThPh which is range, 2.629(4) Å. In summary, there are only small differences in the structural parameters for the six N-(2pyridyl)-N'-arylthioureas reported to date.

3.2. Spectral Studies

The UV spectra (DMSO) show one or two bands for PyTuoT, PyTumT and PyTupT, as well as three other pyridyl thioureas reported previously [14], (Table 4) which we assign to a combination of $\pi \rightarrow \pi^*$ transitions from both rings and an $n \rightarrow \pi^*$ of the heterocyclic ring. Other bands involving the thiourea function are evidently obscured by this latter band. In the infrared spectra of PyTuoT, PyTumT and PyTupT we have assigned ν (NH) to medium intensity absorptions in the 3200 cm⁻¹ region and ν (CS) to bands between 800–860 cm⁻¹ range in agreement with the three previously studied thiosemicarbazones [14].

The ¹H NMR spectra show some variation in the shift of the resonance caused by the intramolecular hydrogen bonding N' \underline{H} in the six pyridyl thioureas studied to date. Addition of methyl groups to the pyridyl ring provides greater electron density to the pyridine nitrogen causing a down field shift for the resonance of N'H. In contrast, the *o*-methyl group in PyTuoT, and to a lesser extent PuTumT and PyTupT's methyl groups, appear to weaken the intramolecular hydrogen bond to the pyridyl nitrogen based on the upfield position for N'H compared to the other thoureas in Table 4. This is presumably as a result of these molecules less planar arrangement (i.e., in the solid state the angle between the pyridyl and phenyl planes is 67° for PyTuoT, the largest of these six thioureas). There is a significant upfield shift for the resonance assigned to NH because of methyl groups on the pyridyl ring; methyl groups on the phenyl ring also cause an upfield shift, but of smaller magnitude. Thus, the inductive effect of the methyl groups enriches the electron density in the NH bond

and the more remote methyl groups on the phenyl ring do so to a lesser extent. However, none of the six thioureas show a significant difference in the ¹³C resonance of the thione carbon with differing numbers of methyl groups on either ring. Thus, like the structural parameters, the spectral data are generally very similar for the six N-(2-pyridyl)-N'-arylthioureas studied, the greatest difference involves the chemical shifts of the two N<u>H</u>'s.

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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