

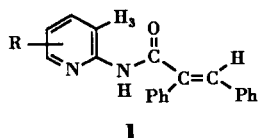
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 Received May 23, 1991

A previous report involving  $^1\text{H}$  nmr spectra of some 1-phenyl and 1-benzoyl 3-(2-pyridyl)thioureas was reinvestigated and found to be incorrect. Analysis of the data permits the designation of preferred conformations for these systems.

*J. Heterocyclic Chem.*, **28**, 2057 (1991).

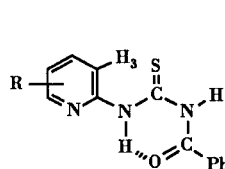
Some time ago, we observed a strong anisotropic deshielding effect on H-3 (on the order of 2 ppm for a typical value of  $\delta$  8.60) in the  $^1\text{H}$  nmr spectra of pyridyl substituted cinnamamide derivatives **1**, which was attributed to a coplanar proximity of the carbonyl group [1]. Recently,



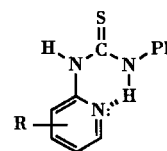
the  $^1\text{H}$  nmr spectral data of some pyridyl substituted thiourea derivatives **2** was reported [2]. While the values presented for the 1-phenyl derivatives [H-3 at  $\delta$  6.97 (**2a**) and 6.67 (**2c**)] suggest a conformation wherein the pyridine ring is not as in **1**, those furnished for the 1-benzoyl derivatives [with H-3 varying from  $\delta$  7.26 (**2h**) to 8.43 (**2f**)] do not allow a reliable interpretation. The unexpected effect of alkyl substitution in the pyridine ring on the chemical shift of H-3 in the latter prompted a reinvestigation of this study.

In addition to the reported 2-pyridyl derivatives, several new ones were prepared according to the furnished procedure. The structures and physical properties of these compounds are given in Table 1. The  $^1\text{H}$  nmr spectral data for **2a-k** is presented in Table 2, where two general trends for H-3 are apparent. Firstly, and in contrast to the previous report, values of H-3 for 1-benzoyl derivatives **2f,h**

**k** appear in the range  $\delta$  8.60-8.84, clearly indicative of a coplanar proximity of C=S. Several values for other hydrogens were also found to be incorrect. The presence of a low field NH absorption ( $\sim$ 13 ppm) shows the existence of intramolecular hydrogen bonding. These findings are consistent with conformation **A**. A second trend for H-3 is observed in the case of 1-phenyl derivatives **2a,c,e**, where in normal values are encountered ( $\delta$  6.72-6.97), in agreement with the previous report. A low field NH absorption ( $\sim$ 13.8 ppm) is observed here also. Conformation **B** is consistent with these findings. The use of a 300 MHz instrument in this study also permitted the observation of a deshielding anisotropic effect on the *ortho* hydrogens of the 1-phenyl group (Table 2), which would be expected for conformation **B**.



**A, 2f, h-k**



**B, 2a, c-e**

In the previous study, a thiol-thione tautomerism was proposed based on the appearance of high field absorption in the  $^1\text{H}$  nmr spectra of these compounds. No evidence of such absorption was found in the present study.

Table 1  
 Physical Properties of New 2-Pyridyl Substituted Thiourea Derivatives 2 R-(2-Py)NHCSNHR'

Compound 2	R	R'	Molecular Formula	Mp °C	Yield %	Reaction Medium	Calcd.			Found		
							C	H	N	C	H	N
<b>b</b>	3-Me	Phenyl	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> S	128-129	90	Benzene	64.17	5.38	17.27	64.56	5.41	16.95
<b>d</b>	5-Me	Phenyl	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> S	176-176.5	90	Benzene	64.17	5.38	17.27	64.16	5.35	17.03
<b>e</b>	6-Me	Phenyl	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> S	181-181.5	90	Benzene	64.17	5.38	17.27	64.10	5.37	16.98
<b>g</b>	3-Me	Benzoyl	C <sub>14</sub> H <sub>13</sub> N <sub>3</sub> OS	126-128	85	Benzene	61.97	4.82	15.49	62.35	4.83	15.80
<b>i</b>	5-Me	Benzoyl	C <sub>14</sub> H <sub>13</sub> N <sub>3</sub> OS	157-159	90	Benzene	61.97	4.82	15.49	62.18	4.88	15.52

Table 2  
<sup>1</sup>H NMR Spectral Data of 2-Pyridyl Substituted Thiourea Derivatives (2) R-(2-Py)NHCSNHR'

Compound	2	R	R'	NH	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	Me	H <sub>o</sub>	H <sub>m</sub>	H <sub>p</sub>
a		H	Ph	9.55 13.69	6.98 (m, +H <sub>5</sub> )	7.60 (m, +H <sub>o</sub> )	6.98 (m, +H <sub>3</sub> )	8.24 (dd, J = 6.0, 1.8)	-	7.65 (d, J = 7.8)	7.42 (t, J = 7.8)	7.25 (t, J = 7.8)
b		3-Me	Ph	8.01 13.80	-	7.52 (d, J = 7.2)	6.94 (m)	8.09 (d, J = 5.1)	2.30	7.69 (d, J = 7.8)	7.40 (t, J = 7.8)	7.25 (t, J = 7.8)
c		4-Me	Ph	9.06 13.80	6.72 (s)	-	6.81 (d, J = 5.1)	8.06 (d, J = 5.1)	2.30	7.68 (d, J = 7.8)	7.40 (t, J = 7.8)	7.25 (t, J = 7.8)
d		5-Me	Ph	9.52 13.70	6.90 (d, J = 8.4)	7.40 (m, +H <sub>m</sub> )	-	8.01 (d, J = 2.1)	2.30	7.67 (d, J = 7.8)	7.41 (t, J = 7.8)	7.25 (t, J = 7.8)
e		6-Me	Ph	9.49 14.12	6.77 (d, J = 8.0)	7.53 (t, J = 8.0)	6.83 (d, J = 8.0)	-	2.50	7.74 (d, J = 7.8)	7.40 (t, J = 7.8)	7.25 (t, J = 7.8)
f		H	COPh	9.13 13.10	8.80 (d, J = 8.4)	7.78 (t, J = 8.4)	7.18 (m)	8.44 (d, J = 4.2)	-	7.90 (d, J = 7.5)	7.51 (t, J = 7.5)	7.60 (t, J = 7.5)
g		3-Me	COPh	9.35 12.37	-	7.60 (m, +H <sub>p</sub> )	7.25 (m)	8.42 (m)	2.41	7.92 (d, J = 7.5)	7.51 (t, J = 7.5)	7.60 (m, +H <sub>4</sub> )
h		4-Me	COPh	9.13 13.10	8.64 (s)	-	7.00 (d, J = 5.1)	8.30 (d, J = 5.1)	2.41	7.90 (d, J = 7.5)	7.54 (t, J = 7.5)	7.64 (t, J = 7.5)
i		5-Me	COPh	9.09 13.04	8.65 (d, J = 8.1)	7.60 (m, +H <sub>p</sub> )	-	8.27 (s)	2.34	7.90 (d, J = 7.5)	7.54 (t, J = 7.5)	7.60 (m, +H <sub>4</sub> )
j		5-Cl	COPh	9.14 13.16	8.84 (d, J = 8.7)	7.71 (dd, J = 8.7, 2.3)	-	8.30 (d, J = 2.3)	-	7.90 (d, J = 7.5)	7.52 (t, J = 7.5)	7.60 (t, J = 7.5)
k		6-Me	COPh	9.09 13.00	8.60 (d, J = 8.4)	7.65 (m, +H <sub>p</sub> )	7.03 (d, J = 7.5)	-	2.53	7.92 (d, J = 7.5)	7.54 (t, J = 7.5)	7.65 (m, +H <sub>4</sub> )

## EXPERIMENTAL

Melting points were determined on a Hoover-Unimelt apparatus and are uncorrected. Elemental analyses were performed by Universidade Estadual de Campinas, Instituto de Química, Brazil. The <sup>1</sup>H nmr spectra were recorded with a Varian Gemini 300 MHz spectrometer in deuteriochloroform with tetramethylsilane (TMS) an internal standard.

All thioureas were prepared according to the general procedure cited in the previous report [2]. The physical properties of unreported derivatives are given in Table 1. The <sup>1</sup>H nmr spectra are presented in Table 2.

## REFERENCES AND NOTES

- [1] A. Kascheres and J. Rodrigues, *J. Org. Chem.*, **40**, 1440 (1975).
- [2] G. Y. Sarkis and E. D. Faisal, *J. Heterocyclic Chem.*, **22**, 137 (1985).