



SYNTHESIS AND CHARACTERIZATION STUDIES OF NOVELPYRIDYLTHIOUREA DERIVATIVES VIA FTIR AND UV-VIS SPECTROPHOTOMETER

NURWAHYUNI AHMAD MUSHTARI & M.SUKERI M. YUSOF

Department of Chemical Sciences, Faculty of Science and Technology, Universiti Malaysia

Terengganu, 21030 Kuala Terengganu. mohdsukeri@umt.edu.my

ABSTRAK

Molekul *N*-2-(3-pikolil)-*N'*-(4-klorobenzoil)tiourea [I], *N*-2-(4-pikolil)-*N'*-(4-klorobenzoil)tiourea [II] dan *N*-2-(5-pikolil)-*N'*-(4-klorobenzoil)tiourea [III] telah berjaya disintesis dan dianalisis menggunakan Fourier Transformasi Infra-Merah (FTIR) dan Spektrofotometer Ultralembayung Cahaya Nampak. Terbitan piridiltiourea mempunyai empat regangan penting, $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C-N})$ dan $\nu(\text{C=S})$ iaitu pada $3291\text{-}3382\text{ cm}^{-1}$, $1670\text{-}1678\text{ cm}^{-1}$, $1327\text{-}1341\text{ cm}^{-1}$ dan $820\text{-}846\text{ cm}^{-1}$ dalam spektrum infra-merah. Dua kromofor utama dalam terbitan tiourea, C=O dan C=S yang terhasil dari peralihan tenaga $n\rightarrow\pi^*$ masing-masing pada penyerapan maksimum 273 nm dan 241 nm.

ABSTRACT

Three new pyridylthiourea derivatives, *N*-2-(3-picolyl)-*N'*-(4-chlorobenzoyl)thiourea (I), *N*-2-(4-picolyl)-*N'*-(4-chlorobenzoyl)thiourea (II) and *N*-2-(5-picolyl)-*N'*-(4-chlorobenzoyl) (III) thiourea have been successfully synthesized and characterized via FTIR and UV-Vis Spectrophotometer. The IR spectra exhibit four interest stretching bands of $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C-N})$ and $\nu(\text{C=S})$ at $3291\text{-}3382\text{ cm}^{-1}$, $1670\text{-}1678\text{ cm}^{-1}$, $1327\text{-}1341\text{ cm}^{-1}$ and $820\text{-}846\text{ cm}^{-1}$, respectively which confirmed the thiourea moieties. There are two vital chromophores, C=O and C=S resulting from $n\rightarrow\pi^*$ transitions have been observed in the UV spectra with maximum absorption at 273 nm and 241 nm, respectively.

Keywords: thiourea, pyridylthiourea, carbonylthiourea

INTRODUCTION

In the last few years, the study of thiourea derivative compounds has recently attracted great interest because of the long-standing unique and versatility role of thiourea derivatives as ligand.

Thiourea and its derivatives have been widely used in research and technological applications such as in the pharmaceutical industry (Dixit et al. 2006) as catalyst in chemical reactions and for extraction of toxic metals using a solid supported liquid membrane system (Quraishi et al. 2002; Ziessel et al. 2006; Fuerst et al. 2005; Wenzel et al. 2002) In addition, thiourea derivatives have been shown to possess antitubercular, antithroid, antihelminthic, insecticidal and rodenticidal properties (Xu et al. 2003; Aaramadaka et al. 2007; Siddiqui et al. 2007; Cunha et al.2007). The interesting coordination properties of thiourea and their important roles in synthetic and pharmaceutical chemistry have turned the attention to investigate the structural properties of pyridylthiourea derivatives (Nguyen et al. 2008).

Furthermore, these compounds are used as ligands in the synthesis of metal complexes. Thiourea and its derivatives are coordinated to a metal ion either by the nitrogen, oxygen or sulphur atom, by any both of them or by other donor atom available in the molecule. These ligands exist either as monodentate, bidentate or polidentate ligand depend to the substituent group present in the molecule. The different donor atoms as well as the various structures of thiourea derivatives result in a variety of complexes (Nguyen et al. 2008; Tadjarodi et al. 2007; Campo et al.2004)

EXPERIMENTAL

Synthesis and instrumentation

All chemicals used were reagent grade quality. 4-chlorobenzoyl chloride (2.80 g, 20 mmol) was dissolved in 20 ml purified dry acetone and was added dropwise into a solution of ammonium thiocyanate (1.52g, 20 mmol) in 30 ml of dry acetone under stirring. Then, 2-amino-3-picoline/2-amino-4-picoline/2-amino-5-picoline (2.16 g, 20 mmol) was added dropwise into the reaction mixture under reflux with continuously stirring for 3 hours. Next, the mixture was poured into a beaker containing some ice blocks. The resulting precipitate was filtered off, washed with cold methanol and dried. FTIR spectra of pyridylthiourea derivatives are obtained in KBR pellets using a Perkin Elmer Spectrometer 100 Series apparatus. Absorption spectra were recorded in cells of *quartz* 1 cm² using a Shimadzu UV-vis spectrophotometer 1601 Series, all compounds are dissolved in pure methanol with the concentration 10⁻⁵ M.

RESULT AND DISCUSSION

FT-IR Spectra

The characteristic $\nu(\text{N-H})$ stretching vibrations of *N,N*-pyridylthiourea derivatives are appeared in the $3291\text{-}3382\text{ cm}^{-1}$ range. This difference between the $\nu(\text{N-H})$ stretching frequencies is due to intramolecular hydrogen bonding (Arslan et al.2009). The strong absorption of $\nu(\text{C=O})$ band in the IR spectra of the compounds are observed in the region $1670\text{-}1678\text{ cm}^{-1}$, apparently decreasing in frequencies comparing with the ordinary carbonyl absorption (1700 cm^{-1}). This is interpreted as being a result of its conjugated resonance with the phenyl ring and the possible formation of intramolecular hydrogen bonding with N-H (Weiqun et al. 2003). In addition, the absorption peak at about 1550 cm^{-1} are attributed to the $\nu(\text{N-C-N})$ stretching vibration. The absorption bands in the range of $1445\text{-}1065\text{ cm}^{-1}$ are assigned to the $\nu(\text{C-N})$ vibrations. The frequencies of 823 cm^{-1} , 804 cm^{-1} and 820 cm^{-1} are assigned to the $\nu(\text{C=S})$ vibration for compound I, II and III respectively. The lowest frequency for $\nu(\text{C=S})$ stretching for compound II indicated that intramolecular hydrogen bonding exists in the compound (Arslan et al. 2009a; Weiqun et al. 2003; Badawi 2009)

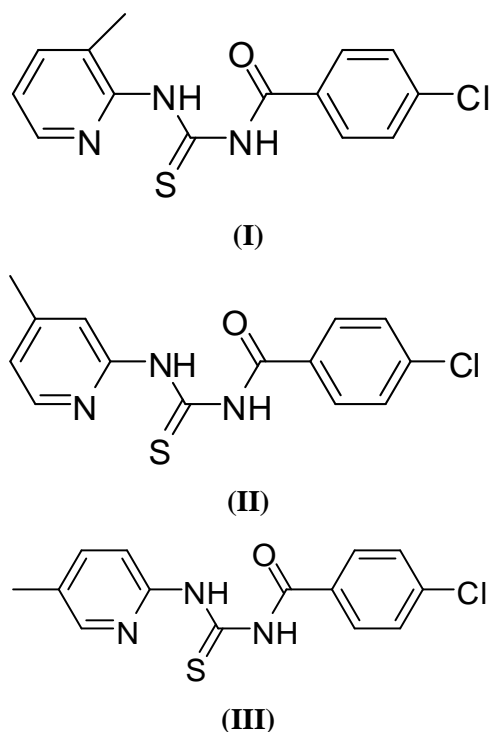


Fig. 1. Molecular structures for compound (I), (II) and (III)

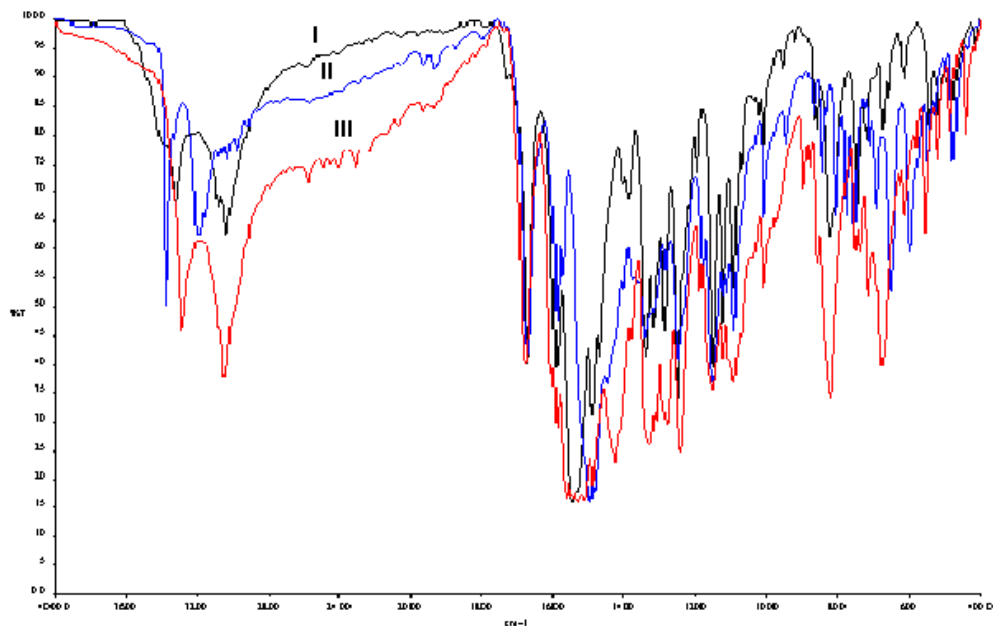


Fig. 2. IR spectra for compound I, II and III

Table 1 Assigned FTIR absorption frequencies

Compounds	ν (cm ⁻¹)				
	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{N-C-N})$	$\nu(\text{C-N})$	$\nu(\text{C=S})$
I	3035	1672	1548	1337	823
II	3187	1670	1494	1341	804
III	3041	1678	1530	1327	820

Absorption spectra

There are two vital chromophores, C=O and C=S resulting from $n \rightarrow \pi^*$ transitions have been observed in the UV spectra with maximum absorption at 273 nm and 241 nm, respectively. The strong absorbance peak presents a red shift in local transition and a broadening of the band with depletion of the structural vibration absorption. It is attributed to the ability of methanol to protonate the oxygen atom of the C=O group or sulfur atom of the C=S group (Yang et al. 2007).

CONCLUSION

Three new pyridylthiourea derivatives have been successfully synthesized via and characterized via FTIR and UV-Vis Spectrophotometer. The results obtained are in agreement with the previously reported data.

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