



Structural study of a novel acetylide-thiourea derivative and its evaluation as a detector of benzene



Wan M. Khairul ^{a,*}, Adibah Izzati Daud ^{a,b}, Noor Azura Mohd Hanifaah ^a, Suhana Arshad ^c, Ibrahim Abdul Razak ^c, Hafiza Mohamed Zuki ^d, Mauricio F. Erben ^e

^a School of Fundamental Science, Universiti Malaysia Terengganu, 21030, Kuala Terengganu, Terengganu, Malaysia

^b Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP), Level 1, Blok S2, Kampus UniCITI Alam, Sungai Chuchuh, Padang Besar, 02100, Perlis, Malaysia

^c School of Physics, Universiti Sains Malaysia, 11800, USM, Penang, Malaysia

^d School of Marine Science and Environment, Universiti Malaysia Terengganu, 21030, Kuala Terengganu, Terengganu, Malaysia

^e CEQUINOR (UNLP, CONICET-CCT La Plata), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962 (1900), La Plata, Argentina

ARTICLE INFO

Article history:

Received 26 December 2016

Received in revised form

16 March 2017

Accepted 16 March 2017

Keywords:

Acetylide

Thiourea

Spectroscopy

DFT

Synthesis

Crystallography

ABSTRACT

The new derivative 1-hexanoyl-3-(4-*p*-tolylethynyl-phenyl)-thiourea (**APHX**) was synthesised by the addition reaction between 4[4-aminophenyl] ethynyltoluene and hexanoyl isothiocyanate in acetone. The acetylide group was incorporated by using Sonogashira cross-coupling reaction allowing for the preparation of acetylide-thiourea compound. **APHX** was then elucidated via single crystal X-ray crystallography analysis, spectroscopic and elemental analysis by Fourier Transform Infrared (FT-IR) spectroscopy, ¹H and ¹³C Nuclear Magnetic Resonance (NMR), UV–visible analysis, CHNS-elemental analysis. **APHX** was also evaluated theoretically via density functional theory (DFT) approach. **APHX** was fabricated onto glass substrate via drop-cast technique prior to act as optical thin-film and its performance as volatile organic compounds (VOCs) sensor was investigated through the difference in UV–vis profile before and after exposure towards benzene. Preliminary findings revealed that **APHX** showed interaction towards benzene with about 48% sensitivity. According to thermogravimetric studies, **APHX** showed good thermal stability, without decomposition up to *ca.* 190 °C. Whilst, crystal structure of **APHX** consists in a nearly planar acylthiourea moiety with the C=O and C=S bonds utilizing *trans* position, favoring by an intramolecular N–H⋯O=C hydrogen bonds. The alkyl chain is oriented 90° with respect to acylthiourea group. The phenyls group in the 1-methyl-4-(phenylethynyl)benzene moieties are mutually planar and slightly twisted with respect to the acylthiourea plane. Centrosymmetric dimers generated by intermolecular N–H⋯S=C and C–H⋯S=C hydrogen bonds forming R₂²(8) and R₁¹(6) motifs are present in the crystals. The interaction between **APHX** with benzene has been modelled and calculated using density functional theory (DFT) via Gaussian 09 software package and the preferred sites of binding are located at the acylthiourea group.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The existence of toxic volatile organic compounds (VOCs) namely toluene, methanol, acetone, and benzene in most workplace environment have resulted the death of many workers who were directly exposed to VOCs over the last century [1]. Benzene particularly is known to be one of the human carcinogenic

substances classified as Group A as both acute and chronic health hazard [2–5] on humans depending on VOCs analyte concentration and time of exposure. It can cause serious health effects in human for instance, eye inflammation, headaches, cancer, and other organ damages [6]. Therefore, there are growing demands to develop class of new gas sensors or at least improving the sensing properties of the existing sensing materials [7,8]. Thus, serious efforts have been actively carried out to propose and develop new active sensing materials with enhanced sensing properties, as alternatives to the existing sensing materials with utmost performances in term of sensitivity, selectivity, and reproducibility.

* Corresponding author.

E-mail address: wmkhairul@umt.edu.my (W.M. Khairul).

In previous occasions, VOCs (benzene) analyte has been detected by carbon nanotubes based materials [9,10], conductive polymeric system [11–13], and metal oxides derivatives [14–16], which needs special treatments like large instrumentation, high operating temperature, and inert environment in order to be operated. Indeed, the developments of alternative, robust and well-defined sensing materials for the detection of VOCs have become the subject of demand in current situation. In this work, we introduce the unique ability of acetylide-thiourea derivative to be employed as active sensing material for VOCs detection. This is due to the benefits of using single-molecular based system in which the molecular framework can be easily designed and tuned to be suited with the selected analyte of interest [17]. It also should be able to operate at room temperature under ambient atmosphere, exhibit ease of synthetic work-up and offer ease of deposition method [18] with high chemical stability [19].

Thiourea derivatives are known as versatile ligands which have ability to bind with metal ions in various coordination modes to form stable complexes [20] depending on various factors such as, conformational isomerism, steric effects, the presence of donor chelating site on the substituent groups and intramolecular interaction. Consequently, this fact on thiourea derivatives have gained interest in the complexation properties of carbonyl (C=O) and thiol (C=S) [21]. For instance, thiourea derivatives resulting as substituted benzoylthiourea introducing acetylide (C≡C) moiety is known to be promising compounds in materials chemistry due to their ability in the formation of intra and intermolecular hydrogen bonds of N–H proton donor group to carbonyl oxygen and sulphur atoms which indeed enhanced the electron rich properties in molecular structures [22].

There are increasing interests in the respect of structural and conformational elucidation of hybrid moieties of thiourea derivatives since they are known as a crucial part for acetylide-thiourea derivatives to be developed as chemosensors either as anion recognition [23] or gas detection [24]. In particular, acetylide-thiourea and gases molecules participate in sensing behaviour via van der Waals interaction [25], indeed playing an important role to act as molecular wires exhibited donor- π -acceptor (D- π -A) properties. In fact, it is well-known that the planar structure of C(O)NHC(S)NH moiety, favoured for acyl/aroyl acetylide-thiourea derivatives, with *trans* orientation between C=O and C=S. Thus, a pseudo six-membered ring is occurred in this conformation, related with the formation of a C=O...H–N intramolecular hydrogen bond.

Both, thiourea and acetylide motifs are commonly been widely investigated in various advanced materials applications [26–29]. Important applications are based on their capacity for electronic transport throughout molecular backbone favoured by rigid π -conjugated systems. In addition, the ability of thiourea derivatives to bind with other targeted analytes such as metals [23] or gas molecules [24] via thione (C=S) or carbonyl (C=O) groups make them applicable as molecular sensors. The presence of lone pair electrons in N, O, and S atoms which implicate the resonance effect of electron delocalisation throughout conjugated molecular system which lead to the active molecular system contained rich electron density properties.

In this contribution, a new derivative containing both acetylide

and thiourea groups, namely 1-hexanoyl-3-(4-*p*-tolylethynylphenyl)-thiourea (**APHX**), see Fig. 1, has been successfully prepared and characterized. **APHX** consists of donor- π -donor (D- π -D) system with hybrid functional substructures including conjugated double and triple bonds together with reactive carbonyl (C=O) and thiocarbonyl (C=S) groups, which supposed to play significant role to afford an ideal interaction with VOCs. Thus, the compound has been further used as active material in the preparation of thin-film onto glass substrate entrapped with PVC for VOCs molecular sensor. Moreover, spectroscopic studies of the fluctuations in electronic transition profiles of the material in the form of thin-film exposed to benzene have been performed. **APHX** has shown to be a good candidate for the detection of benzene in gas phase, with high sensitivity and fast response. To support the findings, the stabilisation energy and interaction geometry between **APHX** and benzene have been modelled by using quantum chemical calculations.

2. Experimental

2.1. Materials

Solvents, chemicals and reagents used in this study namely acetone, acetonitrile, chloroform, dichloromethane, methanol, triethylamine, 4-iodoaniline, ethynyltoluene, palladium(II) chloride, copper(I) iodide, ammonium thiocyanate, and hexanoyl chloride were commercially purchased from local suppliers as analytical reagents such as Fisher Scientific, Merck, HmbG® Chemicals and R&M Chemicals. They were used as received without any further purification carried out. Besides, all reactions involved were executed under an ambient atmosphere without precaution steps to omit humidity during experimental work-up.

2.2. Characterisation and instrumentation

Fourier Transform Infrared (FT-IR) analysis was analysed via Perkin Elmer 100 FT-IR spectroscopy using potassium bromide (KBr) pellets within spectral range 4000–450 cm^{-1} . For structural analysis, ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded in CDCl_3 using Bruker Avance III 400 Spectrometer in the presence of trimethylsilane (TMS) as internal standard in the range δ_{H} 0–15 ppm and δ_{C} 0–200 ppm respectively. In addition, for electronic transition analysis, the compound was characterised via UV–visible analysis using Shimadzu UV–Vis in 1 cm^3 cuvette. Meanwhile, for structural elucidation, the crystallographic structure for X-ray analysis was analysed on Bruker SMART APEXII Duo CCD area-detector diffractometers using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Afterwards, thermogravimetric analysis was carried out using Perkin-Elmer TGA analyzer from 30 to 900 $^{\circ}\text{C}$ at a heating rate 10 $^{\circ}\text{C}/\text{min}$ under nitrogen flow consistently. Lastly, density functional theory (DFT) was calculated for final molecule using Gaussian 09 at the theoretical level of DFT B3LYP/6-31G (d,p) to calculate HOMO-LUMO behaviours as well as to evaluate the stabilisation energy (kJ/mol) and interaction distance between synthesised compound and targeted analyte (benzene).

2.3. Sonogashira cross-coupling reaction: synthesis of 4[4-aminophenyl] ethynyltoluene (**APE**)

Reaction work-up details with respect to the synthesis of precursor (**APE**) followed as stated in the previous literature [24]. Into a 100 ml round bottom flask was charged 4-iodoaniline (3.0 g, 13.7 mmol), ethynyltoluene (3.28 ml, 25 mmol), triethylamine (10 mL), and water as a solvent (30 mL) via $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$ -catalysed (0.05 mmol%). The flask was put at reflux to 180 $^{\circ}\text{C}$ for 24 h. The reaction was monitored by using thin layer chromatography

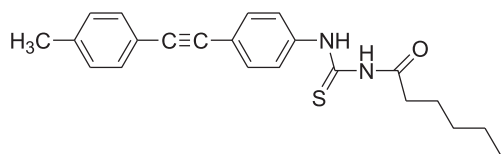


Fig. 1. Molecular structure of **APHX**.

Download English Version:

<https://daneshyari.com/en/article/5161281>

Download Persian Version:

<https://daneshyari.com/article/5161281>

[Daneshyari.com](https://daneshyari.com)