

Short Note

1,3,1',3'-(Dinaphthalene-1,8-diyl)bisthiourea

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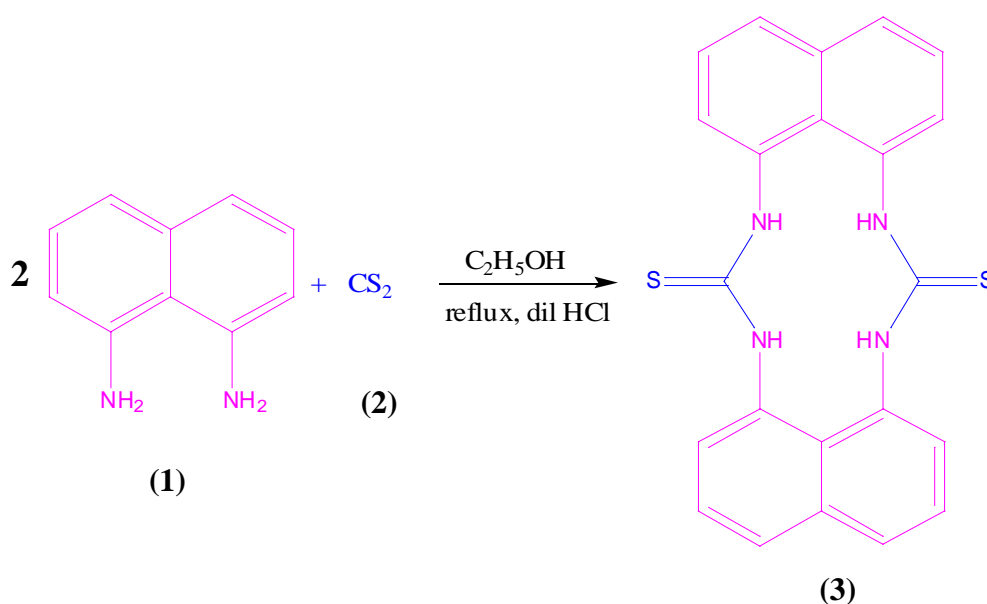
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Abstract: A new bisthiourea compound, 1,3,1',3'-(dinaphthalene-1,8-diyl)bisthiourea, was synthesized. Its structure was characterized by elemental analysis, FT-IR and ^1H -, ^{13}C -NMR and MS spectroscopic techniques. The compound was found to selectively recognize fluoride anions among other halides as demonstrated by means of UV-vis absorption spectroscopic data and the naked eye.

Keywords: carbon disulfide; 1,8-diaminonaphthalene; bisthiourea

1. Introduction

Thioureas are a class of the organic compounds containing sulfur with the general formula $\text{Ar} > \text{N}-\text{C}(\text{S})-\text{N} < \text{Ar}$ or $\text{R} > \text{N}-\text{C}(\text{S})-\text{N} < \text{R}$. These may be mono-thiourea or bis-thiourea derivatives depending the extent of the primary or secondary amines as well as mono- or diamines [1,2]. Some thiourea derivatives are widely used in many fields including the pharmaceutical industry due to their biological properties such as antimicrobial, antibacterial, antifungal, anticancer activity, etc. [3–9]. Recently, compounds of thiourea in coordination with metal complexes have been reported by many researchers, including nonlinear optical (NLO) materials [10,11]. Urea or thiourea derivatives connected with a series of chromogenic and fluorogenic substituents proved to be very efficient for anion sensors. Therefore, a variety of receptors containing one or more urea/thiourea subunits have been designed and tested for anion recognition and sensing over the past years [12–14].

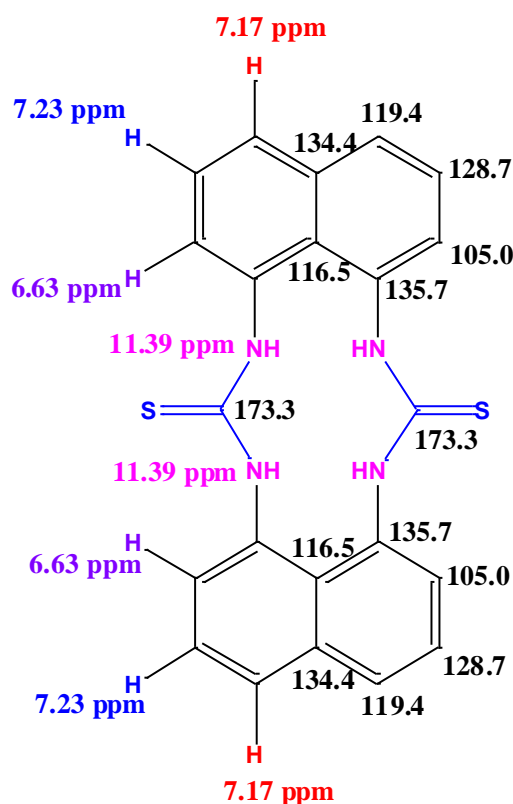


Scheme 1. Synthesis of 1,3,1',3'-(dinaphthalene-1,8-diyl)bisthiourea.

In this paper, a new bithiourea compound named 1,3,1',3'-(dinaphthalene-1,8-diyl)bithiourea was synthesized and its structure was characterized by elemental analysis, FT-IR and ^1H -, ^{13}C -NMR and MS spectroscopic techniques (Scheme 1). A colorimetric sensor, which could selectively detect F^- based on the distinct color change among other halide anions, was investigated in DMSO solution.

2. Results

The title compound, 1,3,1',3'-(dinaphthalene-1,8-diyl)bithiourea, was synthesized and characterized by elemental analysis, IR and ^1H - and ^{13}C -NMR spectroscopic analysis. The FT-IR data of the compound showed two N-H stretching bands at 3411 and 3326 cm^{-1} . The peaks at 3030, 2968 cm^{-1} and 1508 cm^{-1} in the IR data were confirmed as the aromatic C-H and C=C stretching bands, respectively. The strong peak at 1599 cm^{-1} was assigned to the N-H bending band. In addition, the strong band at 1353 cm^{-1} was confirmed in presence of the amido ($=\text{C}-\text{N}$ -) stretching vibration. The very intense peak at 768 cm^{-1} showed C-N asymmetric stretching. The strong bands observed at 1299 and 716 cm^{-1} were assigned to thioureido N-C=S and C=S stretching vibrations, respectively (Figure S1). In ^1H -NMR spectrum, the compound exhibited broad signals at 11.39 ppm (1H, s) which were assigned to the NH-C(S) protons. Generally, the NMR signals of NH protons for thioamides are observed in the range of 9–10 ppm. The chemical shifts of protons on the symmetric naphthalene ring were observed at 7.23 (q, 3,6,3',6'-positions), 7.17 (dd, 4,5, 4',5'-positions) and 6.63 (dd, 2,7, 2',7'-positions) ppm, because the compound consists of two naphthalene units (Figures S2 and S3). In the ^{13}C -NMR signals, chemical shifts for the naphthalene ring carbons were observed at 105(C_2), 116(C_6), 119(C_4), 128(C_3), 134(C_5) and 135(C_1) ppm. The carbon atoms of thiocarbonyl ($\text{C}=\text{S}$) in the symmetric thiourea structure appeared at 173 ppm (Figures S4 and S5) (Scheme 2) (see Supplementary Material).



Scheme 2. ^1H and ^{13}C -NMR chemical shift of the title compound in $\text{DMSO}-d_6$.

The binding behavior of the compound as a receptor with halide ions such as F^- , Cl^- , Br^- and I^- was first monitored by visual observation in DMSO. Upon the addition of F^- to receptor, a prominent change was observed in the UV-Vis absorption spectra. In contrast, the addition of an excess of tetrabutylammonium salt of Cl^- , Br^- and I^- did not cause any notable spectrum changes (Figure 1a). While a color change in the presence of F^- was observed, which also could be detected by the naked eye, an insignificant change in color was observed in the presence of Cl^- , Br^- and I^- (Figure 1b).

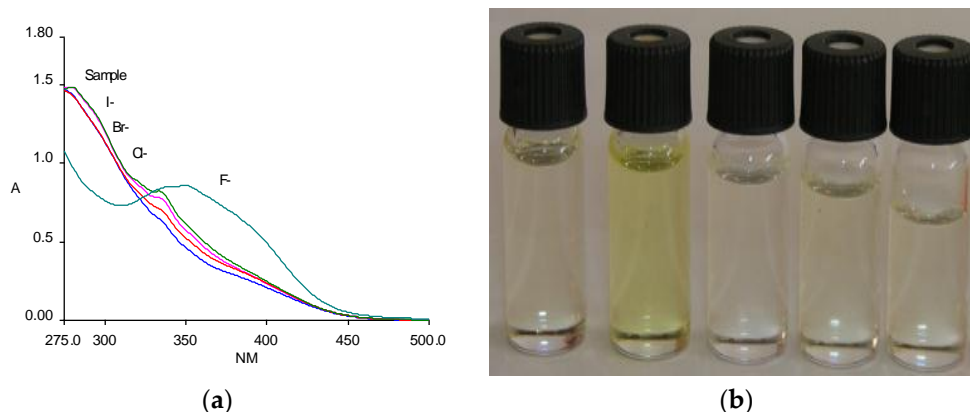


Figure 1. (a) UV-vis absorption changes of compound **3** (0.01 mM) upon addition of tetrabutylammonium salt of halides in DMSO; (b) The color changes of compound (**3**) in DMSO solution (0.01 mM), from left to right, upon addition of 1 equiv. of tetrabutylammonium ions; free, F^- , Cl^- , Br^- and I^- .

3. Experimental Section

3.1. Materials and Measurements

All reagents for synthesis were obtained commercially and were used without further purification. The 1H - and ^{13}C -NMR spectra were recorded in $DMSO-d_6$ at 25 °C on a Bruker NMR spectrometer (Bruker, Mainz, Germany) operating at 400 and 101.6 MHz. Infrared absorption spectra was obtained by a Perkin Elmer BX II spectrometer (PerkinElmer Inc. Waltham, MA, USA) and reported in cm^{-1} units and UV-vis absorption spectra was obtained Lambda-25 (double-beam) spectrometer (PerkinElmer Inc.). MS spectra was recorded using an Agilent 5973 Inert Mass Selective Detector (Agilent Technologies, Santa Clara, CA, USA) equipped with Direct Insertion Probe. Melting point (m.p.) was measured in an Electro Thermal IA 9100 instrument (Electrothermal, UK) using a capillary tube. Thin-layer chromatography was carried out on Merck aluminium sheets (Merck, Darmstadt, Germany) coated with silica gel 60 F₂₅₄.

3.2. Synthesis of 1,3,1',3'-(Dinaphthalene-1,8-diyl)bisthiourea **3**

A solution of carbon disulfide (1.0 g, 0.8 mL, 1.2 mmol) in absolute ethyl alcohol (20 mL) was placed in a 250 mL round-bottomed flask provided with an efficient double surface condenser and a solution of 1,8-diaminonaphthalene (1.58 g, 10 mmol) in absolute ethyl alcohol (20 mL) was added dropwise to the reaction flask. After the absorption apparatus connected to the top of the condenser was placed in the fume cupboard, the reaction mixture was heated under reflux. The progress of the reaction was monitored by TLC analysis. After the completion of the reaction, for 4 h, the excess of carbon disulfide and alcohol was removed by distillation by using a rotary evaporator. The crude grey product was washed several times with dilute hydrochloric acid (1:10) to remove any amine. Precipitate was collected by filtration, after drying, it was purified by recrystallized from acetone/tetrahydrofuran mixture (1:1). The product was obtained as colorless crystals, yield: 2.98 g, 74%; 212–214 °C (dec.),

FT-IR (ATR): 3411, 3326, 3030, 2968, 1599, 1508, 1353, 1299, 768 and 716 cm^{-1} . ^1H -NMR (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 7.23 (q, 1H, C-H), 7.17 (dd, 1H), 6.63 (dd, 1H), 11.39 (s, 1H); ^{13}C -NMR (100 MHz, $\text{DMSO-}d_6$) δ (ppm): 105, 116, 119, 128, 134, 135, 173; MS (EI): (m/z) = 400.1 ($M + 1$); Anal. Calc. For $\text{C}_{22}\text{H}_{16}\text{N}_4\text{S}_2$: C, 65.97; H, 4.03; N, 13.99; S, 16.01 Found: C, 66.31; H, 4.26; N, 13.16; S, 16.27.

Supplementary Materials: The following are available online at www.mdpi.com/1422-8599/2016/4/M917, Figures S1–S5 (FT-IR, ^1H -NMR, ^{13}C -NMR spectrums of compound 3).

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Conflicts of Interest: The authors declare no conflict of interest.

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