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Short Note

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

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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-, 13C-NMR and MS spectroscopic techniques.

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

1. Introduction

Thioureas is the class of the organic compounds having sulphur with the general formula Ar>N-C(S)-N<Ar) or R>N-C(S)-N<R). These may be mono-thiourea or bis-thiourea derivatives depending the extent of primary and secondary amine as well as mono- or diamine. [1-2]. Some thiourea derivatives are widely used in many fields including pharmaceutical industry due to their biological properties such as antimicrobial, antibacterial, antifungal, anticancer, etc [3-10]. Recently, compounds of thiourea in coordination with metal complexes have been reported by many researchers such as NLO materials. [11-13]

In this paper, a new bisthiourea compound as named 1,3,1',3'-(dinaphthalene-1,8-diyl)bisthiourea was synthesized and its structure was characterized by elemental analysis, FT-IR and 1H-, 13C-NMR and MS spectroscopic techniques (Scheme 1).

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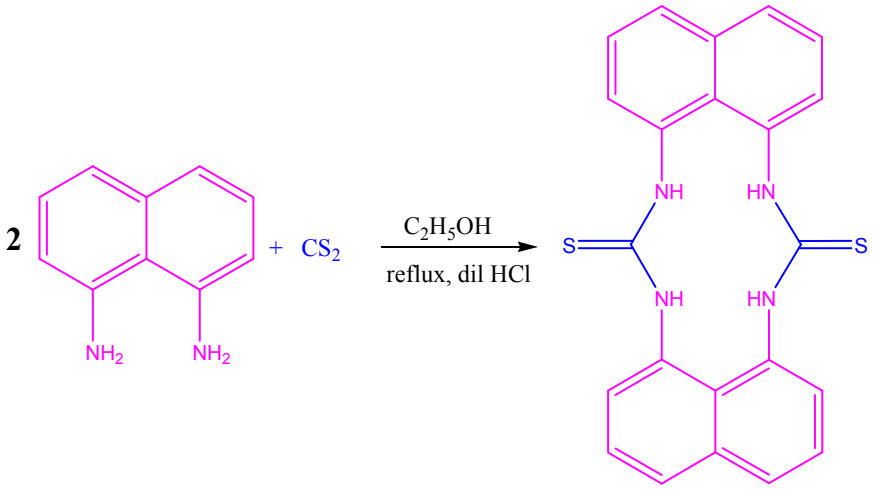

Scheme 1. Synthesis of 1,3,1',3'-(dinaphthalene-1,8-diyl)bisthiourea

2. Results

The title compound, 1,3,1',3'-(dinaphthalene-1,8-diyl)bisthiourea, was synthesized and characterized by elemental analysis, IR and ^{1}H- and ^{13}C-NMR spectroscopic analysis. The IR data of the title 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 the aromatic C-H and C=C stretching bands, respectively. The strong peak at 1599 cm^{-1} was assigned N-H bending band. In the addition to, the strong band at 1353 cm^{-1} was confirmed the amido (=C-N-) stretching vibration. Very intense peak at 768 shows the 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 (Fig 1). 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 title compound contains of two naphthalene units (Fig 2,3). In the 13C-NMR signals, chemical shifts for the naphthalene ring carbons were observed at 105(2), 116(6), 119(4), 128(3), 134(5) and

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135(1) ppm from spectrum signals. The carbon atoms of thiocarbonyl (C=S) in the symmetric thiourea structure was appeared at 173 ppm. (Fig 4,5), (Scheme 2.).

3. Experimental Section

3.1. Materials and Measurements

All reagents for synthesis were obtained commercially and were used without further purification. The ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-*d6* at 25 °C on a Bruker NMR spectrometer operating at 400 and 101.6 MHz. Infrared absorption spectra was obtained by a Perkin Elmer BX II spectrometer and reported in cm^{-1} units. Melting point (m.p.) was measured in an Electro Thermal IA 9100 instrument using a capillary tube. Thin-layer chromatography was carried out on Merck aluminium sheets coated with silica gel 60 F_{254}.

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

A solution of carbon disulphide (1.0 g, 0.8 mL, 1.2 mmol) in absolute ethyl alcohol (20 mL) was placed in a 250 mL round-bottommed flask provided with an efficient double surface condenser and a solution 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 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 disulphide and alcohol was removed by rotary evaporation. 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/tetrahydrofurane mixture (1:1). The product was obtained as courless crystals, 212-214 °C (dec.), FT-IR (ATR): 3411, 3326, 3030, 2968, 1599, 1508, 1353, 1299, 768 and 716 cm-1; 1H-NMR (400 MHz, DMSO-*d6*) δ(ppm): 7.23 (q, 1H, C-H), 7.17 (dd, 1H), 6.63 (dd, 1H), 11.39(s, 1H); 13

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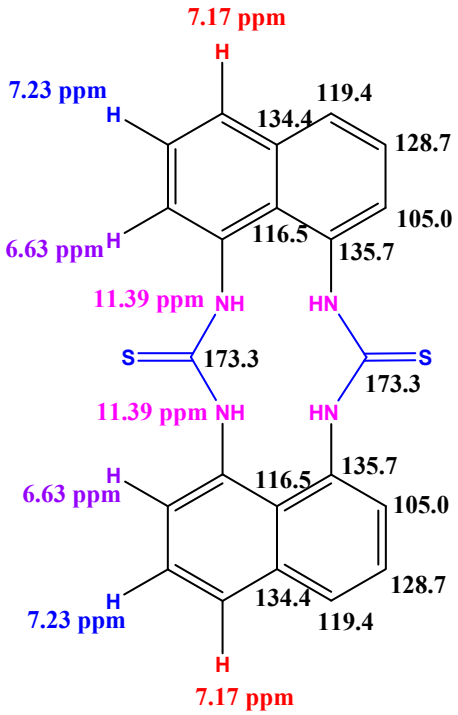
C-NMR (100 MHz, DMSO-*d6*) δ(ppm): 105, 116, 119, 128, 134, 135, 173; MS (EI): *(m/z)* = 400.1 (M+1); Anal. Calc. For $C_{22}H_{16}N_4S_2$: C, 65.97; H, 4.03; N, 13.99; S, 16.01 Found: C, 66.31; H, 4.26; N, 13.16; S, 16.27.



Scheme 2. ^{1}H and ^{13}C NMR chemical shift of the title compound in DMSO-*d6*

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References

1. Katritzky, A.R.; Kirichenko, N.; Rogovoy, B.V. Synthesis of mono- and N,N-disubstituted ureas. *Arkivoc*, **2003**, viii, 8-14.
2. Biaolin, Y.; Zhaogui, L.; Mingjun, Y.; Jiancun, Z. An efficient method for the synthesis of disubstituted thioureas via the reaction of N,N'-di-Boc-substituted with alkyl and aryl amines under mild conditions. *Tetrahedron Lett.* **2008**, 49, 3687-3690.
3. Silvio, C.; Fernando, C.M.Jr.; Giselle, A.N.C.; Manoel, T.R.Jr.; Rosival, B.V.V.; Lourdes, C.S.N.; Ivo, V.; Carlito L.; Fernando P.S. Antimicrobial activity and structural study of disubstituted thiourea derivatives. *Monatshefte fur Chemie* **2007**, 138, 511-516.

4. Khalid, M.K.; Farzana, N.; Muhammad, T.; Ajmal, K.; Shahnaz, P.; Muhammad, I. C.; Wolfgang, V. Synthesis and in vitro urease inhibitory activity of N,N′-disubstituted thioureas. *Eur. J. Med. Chem.* **2014**, 74, 314-323.
5. Azeem, S.; Ataf, A.A.; Ashfaq, M.Q.; Amin, B. Thiourea derivatives in drug desing and medicinal chemistry: A short review. *J. Drug Design and Med. Chem.* **2016**, 2(1), 10-20.
6. Taracad, K.V.; Sanjive, Q.; Peter, S.; Fatih, M.U. Inhibition of mast cell leukotriene release by thiourea derivatives. *Bioorg. Med. Chem, Lett.* **2003,** 13, 485-488.
7. Truong, P.; Thai, K-M.; Nguyen, Thi V.H.; Huynh Thi, N.P. Synthesis and antifungal activites of phenylenedithioureas. *Bioorg. Med. Chem. Lett.* **2004**, 14, 653-656.
8. Jennifer, C.S.; Jae W.C.; Robert, C.; Mark, A.S.; Jann N.S.; Abdul, F.; Richard, J.B. A novel synthetic 1,3-phenyl bis-thiourea compound targets microtubule polymerization to cause cancer cell death. C*ancer Biol. Ther.* **2014**, 15(7), 895-905.
9. Gary, M.C.; Robert, E.D.; James, B.E.; Dennis, S.F. and James R. P. Jr. 1-Hydroxyalkyl-3-phenylthioureas as novel HDL-elevating agents. *Bioorg. Med. Chem, Lett.* **2005**, 15, 809-812.
10. Bianca, K.V.; Jandeli, N.; Janette, S.; Shiy, K.S.; Ross, J.B.; Patrick, M.W.; Lyn-Marie, B. Discovery of novel alkylated (bis)urea and (bis)thiourea polyamine analogues with potent anti-malarial activities. *J. Med. Chem.* **2011**, 54(19), 6624-6633.
11. Muhammad, H.; Muhammad, A.H.N.; Maria, V.B.; Jamshed, I.; Alexander, R.; Bernhard, K.K.; Christian, G.H. Ruthenium II(η6-arene) complexes of thiourea derivatives: Synthesis, characterization and urease inhibition. *Molecules* **2014**, 19, 8080-8092.
12. Muthu, K.; Meenatchi, V.; Rajasekar, M.; Aditya, P.; Meena, K.; Agilandeshwari, R.; Kanagarajan, V.; Meenakshisundaram, S.P. Combined theoretical and experimental studies on the molecular structure, spectral and hirshfeld surface studies of NLO tris(thiourea)zinc(II) sulfate crystals. *J. Mol. Struct.* **2015**, 1091, 210-221.
13. Sivakumar, N.; Kanagathara, N.; Varghese, B.; Bhagavannarayana, G.; Gunasekaran, S.; Anbalagan, G. Structure, crystal growth, optical and mechanical studies of poly bis(thiourea) silver (I) nitrate single crystal: a new semi organic NLO material. *Spectrochim. Acta A* **2014**, 118, 603-613.