



Structural and vibrational study on *N*-(biphenyl-2-thiocarbamoyl)-4-phenylcarboxamide

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ABSTRACT

A new thiourea derivative, *N*-(biphenyl-2-thiocarbamoyl)-4-phenylcarboxamide, is synthesized and characterized by elemental analysis, FTIR, NMR and the single crystal X-ray diffraction study. The title compound crystallizes with two molecules in the asymmetric unit. The dihedral angle between the two aromatic rings in the biphenyl unit is 47.9(2) and 56.52(19)°, respectively, for the two molecules in the asymmetric unit. The molecular conformation is stabilized by intramolecular N–H···O hydrogen bond. The crystal packing shows that the molecules form centrosymmetric dimers connected by N–H···S hydrogen bonds. The vibrational properties have been studied by FTIR and FT-Raman spectroscopy along with quantum chemical calculations at the B3LYP/6-311 + G* level of approximation. The main normal modes related with the thioamide bands are discussed.

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1. Introduction

Various biphenyl derivatives are used in the synthesis of pharmaceuticals, antifungal agents like bifonazole, optical brightening agents, dyes and polychlorinated biphenyls (PCBs). The rotation around the single bond in biphenyls, and in particular the ortho-substituted ones, is sterically hindered. Therefore, some substituted biphenyls exhibit the atropisomerism; specifically, the individual C₂-symmetric-isomers are optically stable. Some derivatives, as well as related molecules such as 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), find application as ligands in asymmetric synthesis [1]. The relationship between ligand conformations and complexation properties in some homoditopic biphenyl thioureas has been demonstrated [2]. Some biphenyl thioureas having structure very closely related to that of title compound have been used as organocatalysts for electrochemical reductions [3]. Other biphenyl thioureas have been used in carboxylate sensing and the effect of the ligand substituents on the geometry of the complexes has been reported [4]. Biphenyls thiourea derivatives are also potent Vitronectin receptor antagonists [5] and thiourea-based molecular clips has been used for fluorescent discrimination of isomeric dicarboxylates [6]. Moreover, the hydrogen-bonding ability of the thiourea moiety has extensively been used in

construction of anion receptors [7–9] and in the thiourea-based metal complexes [10] and organocatalysts [11]. In particular, arylthioureas have been successfully used in environmental control, as ionophores in ion selective electrodes [12–14]. Very recently, the structural and conformational properties of *N*-(diethylcarbamothioyl)benzamide in different phases, before and after the interaction with a heavy metal ion were studied and the behavior of the molecule as a ionophore in a typical ion selective electrode membrane has been simulated [15].

Herein, the synthesis, characterization and vibrational properties, together with the X-ray molecular structure of *N*-(biphenyl-2-thiocarbamoyl)-4-phenylcarboxamide is reported. Some related structures containing the biphenyl moiety as a part of thiourea nucleus include the *N*-(biphenyl-4-carbonyl)-*N'*-(4-chlorophenyl)-thiourea [16], its 2-chloro- [17], 2-pyridyl methyl- [18], and recently reported 6-methylpyridin-2-yl [19] analogs but in all of these compounds the biphenyl moiety is derived from the corresponding isothiocyanate, whereas in present case it is obtained from the corresponding anilino compound.

2. Experimental

2.1. Synthesis

A solution of 2-aminobiphenyl (1.5 mmol) in 20 ml dry acetonitrile was added dropwise to a two-necked round-bottomed flask

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containing an equimolar amount of benzoyl isothiocyanate (1.5 mmol) in 20 ml of acetonitrile. The mixture was refluxed for 3 h. On cooling, the reaction mixture was acidified with dilute hydrochloric acid. The solid product obtained on filtration was washed with water and recrystallized from an acetone:dichloromethane mixture (1:2). Colourless crystals were obtained on slow evaporation (yield 91%, m.p.: 126–127 °C). Anal. Calcd. for $C_{20}H_{16}N_2OS$: C, 72.26; H, 4.85; N, 8.43; S, 9.65. Found: C, 72.01; H, 4.69; N, 8.41; S, 9.57%. 1H NMR (300 MHz, $CDCl_3$, δ , ppm): 12.31 (s, 1H, CONH), 9.22 (s, 1H, CSNH), 7.14 (t, 1H, $J = 2.1$ Hz, bp), 7.33–7.40 (m, 4H, bp), 7.36 (m, 4H, bp), 7.66 (dd, 1H, $J = 4.8$, 2.1 Hz, ph), 8.09–8.22 (m, 2H, ph), 8.40–8.48 (m, 2H, ph). ^{13}C NMR (75 MHz, $CDCl_3$, δ , ppm) 115.83, 116.13, 117.04, 117.35, 118.55, 123.35, 123.65, 124.41, 126.27, 126.38, 128.90, 129.87, 130.87, 137.04, 141.35, 149.80, 159.51, 162.71, 168.39 (C=S), 172.89 (C=O).

2.2. Crystal structure determination

$C_{20}H_{16}N_2OS$, $M_r = 332.41$, colorless crystal, size $0.36 \times 0.33 \times 0.29$ mm³, triclinic space group P-1, $a = 10.2091(7)$, $b = 10.9563(6)$, $c = 15.7563(10)$, $\alpha = 84.103(5)$, $\beta = 77.217(5)$, $\gamma = 89.164(5)$, $V = 1709.57(19)$, $Z = 4$, $D_{calc} = 1.291$ g/cm³, $F(0\ 0\ 0) = 696$, $\mu = 0.202$ mm⁻¹. STOE IPDS-II diffractometer [20] using Mo K α radiation ($\lambda = 0.71073$ Å) at $T = 173$ K. An absorption correction was applied using the MULABS [21] option in PLATON [22]. The structure was solved by direct methods [23] and refined by full-matrix least-squares using SHELXL-97 against F^2 using all data [23]. All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.95 Å (aromatic CH) and 0.98 Å (methyl groups) from the parent C atoms; a riding model was used during the refinement process and the $U_{iso}(H)$ values were constrained to be $1.2U_{eq}(\text{aromatic C})$ or $1.5U_{eq}(\text{methyl C})$. The H atoms bonded to N were freely refined. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data CCDC-745277 can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk]. Any request to the CCDC for this material should quote the full literature citation and the reference number 745277.

2.3. Vibrational spectroscopy

Solid-phase IR spectra were recorded as KBr discs with a resolution of 2 cm⁻¹ in the 4000–400 cm⁻¹ range on a Bruker EQUINOX 55 FTIR spectrometer. The FT-Raman spectrum was recorded in the region 4000–100 cm⁻¹ using a Bruker IFS 66v spectrometer equipped with Nd:YAG laser source operating at 1.064 μ m line with 200 mW power of spectral width 2 cm⁻¹.

2.4. GC–MS determination

The GC–MS measurements were recorded in a GCMS-QP2010 SHIMADZU instrument using gaseous Helium as mobile phase with the pressure in the column head equal to 100 kPa. The column used was a 19091J-433 HP-5 of 30 m \times 0.32 mm \times 0.25 mm film thickness. A 1 μ L volume of the compounds dissolved in $CHCl_3$ was chromatographed under the following conditions: injector temperature was 210 °C, the initial column temperature (100 °C) was held for 3 min, then increased to 200 °C at 20 °C/min and held for 2 min after elevated to 300 °C at 35 °C/min and held for 2 min. In the spectrometer the source was kept at 200 °C. One peak at retention time 8.5 min is observed in the chromatogram, with a fragmentation pattern dominated by the following peaks: 211 (100%, $C_{12}H_9NCS^+$), 178 (86%, $C_6H_5CONHCSN^+$), 151 (35%, $C_{12}H_7^+$) and 105 (12%, $C_6H_5CO^+$).

2.5. Quantum chemical calculations

The molecular geometries were optimized to standard convergence criteria and harmonic frequencies calculated by using DFT hybrid method with Becke's non-local three parameter exchange and the Lee, Young and Parr correction (B3LYP) using the 6-311 + G* basis sets as implemented in the GAUSSIAN 03 program package [24].

3. Results and discussion

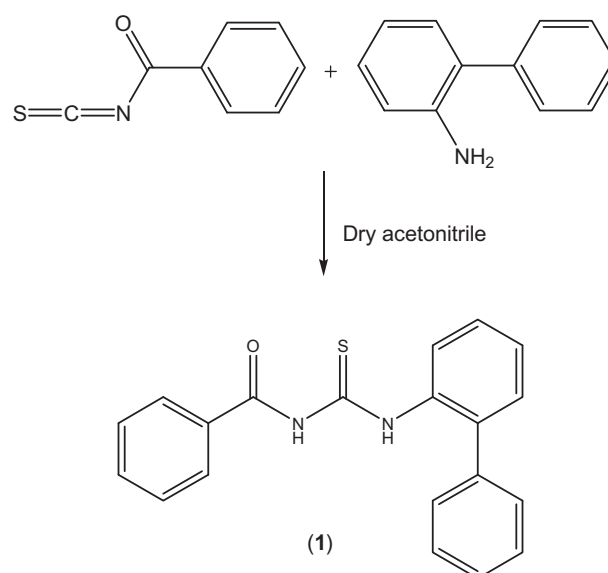
3.1. Synthesis

The synthetic pathway to N-(biphenyl-2-thiocarbamoyl)-4-phenylcarboxamide, (I) is shown in Scheme 1. Thus benzoyl isothiocyanate was produced *in situ*, by reaction of freshly prepared benzoyl chloride with an equimolar amount of potassium thiocyanate in dry acetonitrile. Treatment of the latter with equimolar quantity of 2-aminobiphenyl afforded the title compound (I). Colourless crystals suitable for the X-ray diffraction study were obtained on slow evaporation from an acetone: dichloromethane mixture (1:2).

In the 1H NMR spectrum of the compound in addition to the signals for aromatic protons, the characteristic N–H singlets at δ 12.31 for CONH and 9.22 for CSNH ppm and in ^{13}C NMR the peaks for carbonyl and thiocarbonyl were observed δ 172.89 and 168.39 ppm respectively.

3.2. X-ray structure

The title compound crystallizes with two crystallographically independent molecules in the asymmetric unit. Table 1 includes selected geometric parameters derived from the structure refinement, as well as those obtained from quantum chemical calculations. The dihedral angle between the two aromatic rings in the biphenyl unit is 47.9(2) and 56.52(19)° for the two molecules in the asymmetric unit, respectively. Also the orientation of the C=O and the phenyl ring in the benzoyl group shows a slightly different orientation when both molecules are compared (see Table 1). The X-ray molecular structures of the two crystallographically independent molecules are shown in Fig. 1.



Scheme 1. Synthetic pathway to N-(biphenyl-2-thiocarbamoyl)-4-phenylcarboxamide.

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