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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 $56.52(19)^\circ$, 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 thioureabased 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, aroylthioureas 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 recrystalized from an acetone:dichloromethane mixture (1:2). Colourless crystals were obtained on slow evaporation (yield 91%, m.p.: 126-127 °C). Anal. Calcd. for C₂₀H₁₆N₂OS: 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, CDCl₃ 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). ¹³C NMR (75 MHz, CDCl₃, 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 × 0.33 × 0.29 mm³, triclinic space group P-1, *a* = 10.2091(7), $b = 10.9563(6), c = 15.7563(10), \alpha = 84.103(5), \beta = 77.217(5), \gamma = 10.9563(6), c = 15.7563(10), \alpha = 10.9563(5), \beta = 10.9563(5), \gamma = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563(6), \beta = 10.9563(6), \gamma = 10.9563(6), \beta = 10.9563($ 89.164(5), V = 1709.57(19), Z = 4, $D_{calc} = 1.291 \text{ g/cm}^3$, $F(0\ 0\ 0) =$ 696, $\mu = 0.202 \text{ mm}^{-1}$. STOE IPDS-II diffractometer [20] using Mo K α radiation (λ = 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 Uiso(H) values were constrained to be 1.2U_{eq}(aromatic C) or 1.5U_{eq}(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 × 0.32 mm × 0.25 mm film thickness. A 1 μ L volume of the compounds dissolved in CHCl₃ 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%, C₁₂H₉NCS⁺), 178 (86%, C₆H₅CONHCSN⁺), 151 (35%, C₁₂H₇⁺) and 105 (12%, C₆H₅CO⁺).

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)-4phenylcarboxamide, (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 CON*H* and 9.22 for CSN*H* ppm and in ¹³C 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 $56.52(19)^{\circ}$ 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.

Table 1

Selected experimental and calculated geometrical parameters (values in Å and degrees) for the central -C(O)NHC(S)NH- moiety for the title species.

Parameter ^a	Experimental		B3LYP/6-311 + G*
	Molecule A	Molecule B	
C=0	1.2321(16)	1.2302(16)	1.225
C=S	1.6661(14)	1.6777(14)	1.673
C2—N2	1.3291(17)	1.3289(17)	1.344
C2-N1	1.4034(16)	1.3979(16)	1.408
C1-N1	1.3761(17)	1.3783(18)	1.383
S=C-N2	124.06(10)	124.57(10)	127.5
S=C-N1	119.72(10)	119.17(10)	117.6
O=C-N1	121.96(12)	122.64(11)	122.7
C1-N1-C2	127.28(12)	127.33(11)	130.0
0=C-N1-C2	0.9(2)	1.0(2)	2.6
N2-C2-N1-C1	5.9(2)	4.3(2)	0.2
0=C-C11-C16	-8.78(19)	32.5(2)	21.7
C23-C22-C31-C32	54.2(2)	44.01(19)	54.2
C21-C22-C31-C36	56.52(19)	47.9(2)	55.8

^a For atom numbering see Fig. 1.

The amidic N1–C1 [1.377(2) Å] and thioamide N1–C2 [1.401(2) Å] and N2–C2 [1.329(2) Å] bond lengths (mean values are given) are both shorter than C–N single bond [25], indicating a partial double bond character. This observation indicates that resonance interactions are extended over the whole planar –C(O)NHC(S)NH– moiety, in accordance with the behavior recently reported for thiocarbamate species [26]. Moreover, it is worth noting that a definite trend in the C–N bond distances has been recognized for these species [27], the lengths increasing in



Fig. 1. Molecular structure of the two crystallographically independent molecules in the asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level.

the order C2—N2 < C1—N1 < C1—N2 (see Table 1). This tendency is also reproduced by the quantum chemical calculations (B3LYP/ $6-311 + G^*$, see Table 1) suggesting that intramolecular electronic effects -rather than crystal packing effects- are responsible for the observed N—C bond lengths values.

The molecular structure and conformational flexibility are important properties for determining the donor-acceptor capabilities on thiourea derivatives [28,29]. For example, Fabbrizzi et al. reported that substituted-phenyl urea compounds interacts through hydrogen bonding with a variety of oxoanions to give bright colored complexes [30] and a variety of receptors containing the urea and the thiourea groups have been designed for anion recognition [31]. These effects are closely related with the conformational properties and the presence of intra- and intermolecular hydrogen bonding interactions on the thiourea group [31]. The title species possesses intramolecular and intermolecular hydrogen bonding interactions, as shown in Table 2. In effect, N-benzovl-*N*'-arylthioureas have been thoroughly investigated in connection with the formation of intramolecular hydrogen bonding [32–35]. It was found that the intramolecular hydrogen bond between the oxygen atom in the C=O group and the hydrogen atom of the thiourea group is favored by the formation of a six-membered ring [36,37]. In the title species, the molecular conformation is stabilized by such an N-H...O hydrogen bond. The non-bonding distances O1...N2 and O1A...N2A are 2.616(1) and 2.627(1) Å, respectively in agreement with intramolecular hydrogen bonding found in other N-benzoyl N'-substituted thioureas, which are reported in the range of 2.618(4)-2.654(2) Å [38,39]. Moreover, an intermolecular interaction involving these groups is observed between the crystallographically independent molecules through an N1-H--O1A hydrogen bond, with a N1--O1A distance of 3.045(1) Å.

The patterns of packing adopted by thiourea derivatives were rationalized by McBride et al. [40] in terms of molecular structure, solvent of crystallization, and energies and efficiencies of packing. In the title molecule, the crystal packing shows (Fig. 3) that both crystallographically independent molecules form centrosymmetric dimers connected by N1–H···S (x - 1, y, z) and N1A–H···S (x + 1, y, z) hydrogen bonds, adopting a well-known crystal motif for *N*-benzoyl-thiourea compounds [33,41]. These non-bonding N···S distances are 3.396(1) and 3.625(1) Å, respectively.

3.3. Vibrational analysis

The observed infrared absorptions and the FT-Raman frequencies along with their relative intensities and probable assignments are summarized in Table 3. A tentative assignment of the observed bands was carried out by comparison with spectra of related molecules [42–48]. Very recently, the vibrational properties of the thiourea molecule – the idealized parent species – were revisited by Srinivasan et al. [49]. However, in many case a clear assignment of the observed infrared absorptions and Raman signals to a specific vibration is unclear. To further improve this situation, an assignment of the observed vibrational spectra can be assisted by a systematic comparison with the theoretically calculated one.

Table 2 Hydrogen bonds [Å and $^\circ]$ for the title species.

D—H···A	d(D—H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<(DHA)
N(1)—H(1)···S(1A)#1 [*]	0.872(19)	2.535(19)	3.3957(12)	169.1(16)
N(2) - H(2) - O(1)	0.848(18)	1.969(17)	2.6271(14)	133.7(15)
$N(1A) - H(1A) - S(1)#2^{a}$	0.861(18)	2.780(19)	3.6250(13)	167.3(15)
N(2A)- $H(2A)$ ···O(1A)	0.908(18)	1.891(17)	2.6164(14)	135.3(15)

^a Symmetry transformations used to generate equivalent atoms: #1 x - 1, y, z, #2 x + 1, y, z.

Table 3

Observed and theoretical $(B3LYP/6-311 + G^*)$ vibrational data (cm^{-1}) with a tentative assignment for the title species.

FTIR ^a	Raman ^a	B3LYP/6-311 + G* ^b	Tentative assignment
3289 m. br		3626 (5.9)	v(N1-H)
3135 s br		3421 (49.9)	v(N2-H)
3089 m br	3067	3212-3159 ^c	v(C-H)
1662 s	1662 s	1710 (36.3)	v(C=0)
1601	1602 5	1719 (30.3)	$v(\mathbf{C}=\mathbf{C})$
1601 W	1502 vs	1050	$V(\mathbf{U}-\mathbf{U})$
1581 W	1582 111	1501 (77.0)	S(NO II)
1528 VVS	1538 VW	1591 (77.6)	O(NZ-H)
			Thioamide band I
1509 vvs	1508 m	1563 (100.0)	$\delta(N1-H)$
1492 s.sh	1493 w	$1650 - 1400^{d}$	v(C=C)
1476 s. sh	1477 vw		
1451 m. sh	1455 sh		
1324 s	1324 vw	1377 (90.1)	$v_{ac}(N-C-N)$
			Thioamide band II
			iniounide build if
1267 m, sh	1300 m	1301 (2.6)	v(C22–C31)
1254 m		1266 (27.6)	v(C1-N1)
1229 sh	1255 m	1242 (2.0)	v(C2-N21)
1181 w	1183 w	1213 ^e	δ(CH)
1154 vs	1158 m	1177 (47.6)	$v_{s}(N-C-N)$
			Thioamide band III
1144 110	1146 ch	e	S(C II)
1144 VS	1140 511		∂(C − Π)
1109 W			
1086 W			
10/2 sh			
1049 w	1050 w		
1026 w	1034 m		
1009 w			
999 w	999 vs		
974 w		964 (1.2)	$\delta(CN1C)$
938 w	941 m	958 (1.5)	$\delta(CN2C)$
931 m		931 ^e	$\rho(C-H)$
914 w			
874 vw	875 m		
854 m	854 m	866 (3.8)	$\delta(NCN)$
773 w	775 m	783 (2.5)	v(C=S)
			Thioamide band IV
750		757 (0.2)	
759 W		757 (8.2)	$\rho(C-H)$
/41 m	741 w	/43 (13.4)	$\rho(N2-H)$
720 w	717 m	729	$\delta(CC)$
701 m		697 (4.3)	oop (NCN)
672 m	671 w	661 (4.5)	$\rho(N1-H)$
621 w	615 w	607 (5.1)	oop C=S
552 vw	547 vw	557 ^t	$\rho(CC)$
523 m			
480 w			
451 vw	451 w		
	409 vw		
	348 vw	349 (1.5)	$\rho(C=0)$
	306 w		
	276 m		
	212 m		
	216 m		

^a FTIR of solid in KBr pellets, FT-Raman of finely powdered solid. Band intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak.

^b In parentheses relative band strengths, IR intensities $[100\% \equiv 538 \text{ km/mol}]$.

^c The 14 ν (C–H) stretching modes expected for the molecule are computed in the 3212–3159 cm⁻¹ range as low intensity infrared absorptions.

^d The ν (C=C) stretching modes due to the phenyl rings are computed in the 1650–1400 cm⁻¹ range as low to medium intensity infrared absorptions.

^e Τηε σεωεραλ δ (C–H) deformation and ρ (C–H) rocking normal modes are computed below 1213 and 931 cm⁻¹, respectively.

^f The δ (C–C) and ρ (C–C) appear in the computed IR near 730 and 570 cm⁻¹ as low to medium intensity absorptions.

Quantum chemical calculations and normal coordinate analysis have been applied [36] and recently density functional theory (DFT) methods at the B3LYP/6-31G(d) basis set was used to predict the vibrational frequencies of related species [39,47]. The use of more extended basis set certainly leads to a good performance when substituted benzoylthiourea compounds are analyzed [50]. Thus, the molecular structure of the studied compound has been optimized at the DFT-B3LYP level of approximation by using the triple-zeta $6-311 + G^*$ basis sets. The geometrical parameters are in very good agreement with the experimental ones (see Table 1) and the computed harmonic frequencies are gathered in Table 3.

In the infrared spectra a series of broad absorptions are observed at 3289, 3135 and 3089 cm⁻¹. The 3289 and 3135 cm⁻¹ bands could be assigned to the N–H stretching modes [47,51,26], the red-shifted absorption is most likely due to the v(N2-H)stretching mode, related with the formation of C=O···N–H intramolecular hydrogen bond, as observed in the X-ray analysis. A single well-defined Raman signal is observed at 3067 cm⁻¹, characteristic of the C–H vibrations of the phenyl groups. These features are in agreement with the calculated frequencies (see Table 2), with the v(N2-H) stretching mode computed as an strong intensity band located at lower frequencies than the corresponding v(N1-H) fundamental.

Fig. 2 shows the Raman and IR spectra of the title compound in the 1800–600 cm⁻¹ range. A large number of signals are observed with pronounced overlapping and for the title species, many of these signals result from both the central thiourea moiety as well as from the substituent groups. In the infrared spectrum, the strong 1662 cm⁻¹ (1663 cm⁻¹ Raman) band corresponds to the v(C=O)mode, which is similar in frequency to the C=O···H—N hydrogen bonding found in many small-molecule studies [52]. Calculated (B3LYP/6-311 + G*) frequencies for these fundamental amounts 1719 cm⁻¹. The relative low value observed for the v(C=O) fundamental is in accordance with the presence of a intramolecular C=O···H—N interaction in the —C(O)NHC(S)NH— moiety [53]. Alternatively, this behavior has been also interpreted as being a result of conjugated resonance interactions between the carbonyl and the phenyl ring in *N*-benzoyl substituted thiourea compounds



Fig. 2. FT-Raman and IR spectra (solid) for the title compound in the 1800– 600 cm^{-1} region. The characteristic carbonyl stretching mode and the "thioamide bands" are identified.



Fig. 3. Crystal packing of the title species viewed along [1 0 0] with displacement ellipsoids drawn at the 50% probability level.

[36]. It is worthy to mention that the C=O stretching mode is appreciably coupled with the C-N stretching and with the N-H bending mode, as observed for related compounds [54–56].

In (thio)amide compounds several infrared absorption bands which are called "(thio)amide bands" are important for studying structural and electronic properties because they are sensitive to intermolecular hydrogen bonding and conformational changes [57]. This approach has recently been applied also in the analysis of urethane [57] and thiourea derivatives [53]. In compounds containing the thioamide group give rise to four characteristic vibrational bands, the thioamide bands I, II, III and IV have a large contribution from δ (N–H) (I), ν (C–N) (II and III) and ν (C=S) (IV) motions and are usually reported around 1500, 1300, 1100 and 750 cm⁻¹, respectively [58]. These bands emerge in a region which is plenty of absorptions from substituent groups, making difficult their identification. The joint analysis of both IR and Raman spectra arises necessary for an unambiguous identification [53].

It is well-known that the thiourea group presents characteristic a band in the 1500–1600 cm⁻¹ range of the IR spectrum, originated by the N–H deformation mode $[\delta(N-H)]$. For the title species, a very strong and rather broad absorption with defined maxima at 1528 and 1509 cm⁻¹ can be assigned to the δ (N2–H) (thioamide band I) and $\delta(N1-H)$ modes, respectively. The Raman counterparts are observed as signals of low and medium intensities at 1538 and 1508 cm⁻¹, respectively. B3YLP/6-311 + G^{*} computations predict the presence of strong bands in the infrared spectrum due to the δ (N2–H) and δ (N1–H) normal modes at 1591 and 1563 cm⁻¹, respectively, in reasonable agreement with the proposed assignment. Nevertheless, it should be noted that several v(C=C) stretching modes from the aromatic groups also contribute to absorptions in this region. The strong and medium intensity signals centered at 1602 (1601 cm⁻¹ infrared, weak) and 1582 cm⁻¹ (1581 cm⁻¹ infrared, weak) in the Raman spectrum could be assigned with confidence to symmetric v(C=C) stretching modes.

The region between 1400 and 800 cm⁻¹ in the vibrational spectra of thioureido compounds is usually rich in medium intensity bands from skeletal motions, especially vibrations containing contributions from the v(C-N) motion in the thiourea core [53]. Intense bands can be observed at 1324 and 1154 cm⁻¹ in the IR spectrum of the studied compound with the corresponding counterpart in the Raman spectrum at 1324 and 1158 cm^{-1} as very weak and medium intensity signals, respectively. Taking into account the vibrational properties reported for the simple thiourea molecule [49], it is expected that the C–N stretching modes, which are usually coupled in symmetric and antisymmetric motions, appear in this region [54]. Thus, following the quantum chemical calculation description, the v(NCN) antisymmetric (thioamide band II) and symmetric (thioamide band III) stretching modes of the thiourea moiety, are respectively assigned to these bands. Computed frequency values are 1377 and 1177 cm⁻¹, respectively, both modes displaying strong dipole moment derivatives.

The medium intensity signal at 775 cm⁻¹ in the Raman spectrum, with a weak counterpart in the infrared at 773 cm^{-1} , is tentatively assigned to the thioamide band IV, mainly due to the v(C=S) stretching mode, in agreement with previously studied thiourea derivatives [39,53]. However, it should be mentioned that higher values have been reported for this fundamental. For example, in the parent thiourea molecule, this mode appeared at 1094 cm^{-1} in the infrared spectrum (1105 cm^{-1} Raman) [49], and even higher values – up to 1325 cm^{-1} – have been also reported in related compounds [36,45]. A definite assignment should take into account strong coupling between fundamentals, as reported for simple alkyl derivatives of thiourea, where the C-N and C=S stretching modes contribute to a variety of fundamentals [59]. Moreover, the formation of C=S···H-X intermolecular hydrogen bonds seems to strongly effect the frequency of the v(C=S)mode [42].

4. Conclusion

The title compound was synthesized and characterized by spectroscopic and X-ray diffraction techniques and 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. A strong intramolecular hydrogen bond between the C=O and H–N1 groups forming a 6-membered ring is present in the crystal. From the joint analysis of both IR and Raman spectra the main normal modes related with the thioamide group ("thioamide bands") have been tentatively assigned as follow: 1528 cm⁻¹ [δ (N2–H), thioamide band I], 1324 cm⁻¹ [ν_{as} (N–C–N), thioamide band II], 1154 cm⁻¹ [ν_{s} (N–C–N), thioamide band IV].

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Appendix A. Supplementary material

Tables of atomic coordinates and equivalent isotropic displacement parameters, full intramolecular bond distances and angles, atomic anisotropic displacement parameters and hydrogen atoms positions are given in Tables S1–4. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.molstruc.2010.10.013.

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