# Synthesis, crystal X-ray diffraction structure, vibrational properties and quantum chemical calculations on 1-(4-(4-Fluorobenzamido)phenyl)-3-(4-fluorobenzoyl)thiourea

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### ABSTRACT

The 1-(4-(4-Fluorobenzamido)phenyl)-3-(4-fluorobenzoyl)thiourea species (**1**) has been synthesized and characterized by GC–MS, elemental analyses and ^{1}H NMR and FTIR spectroscopy techniques. The crystal structure of the novel compound – having a benzamide moiety attached to a thiourea nucleus – has been determined by X-ray diffraction. The species crystallize in the triclinic space group P-1, Z = 4, with 2 molecules per asymmetric unit. Additionally there is one ethylacetate solvent molecule per asymmetric unit. The carbonyl and thiourea groups are almost planar and the conformation adopted by the C=S and the C=O double bonds is mutually antiperiplanar. Density functional theory methods have been applied to determine the conformational space around the central –C(O)NHC(S)NH– moiety. 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.

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## 1. Introduction

Fluoro-substituted thioureas are excellent substrates for studying the hydrogen bonding due to their ability to form intra- and intermolecular hydrogen bonds of the N–H proton-donor groups to sulphur and carbonyl oxygen atoms [1–3]. Thus, N-benzoyl-Ń-arylthioureas have been thoroughly investigated in connection with the formation of intramolecular hydrogen bonding [4–7]. In effect, 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 [2,8,9]. Moreover, the hydrogen-bonding ability of the thiourea moiety has extensively been used in construction of anion receptors [10–12] and in the thiourea-based metal complexes [13] and organocatalysts [14]. Very recently, Pisiewicz et al. reported the preparation of a fluorine substituted thiourea which forms heteroleptic monocationic Pd(II), Pt(II) and Ru(II) complexes [15]. Moreover, ion selective electrodes for Pb(II) based on benzoylthioureido derivatives as ionophores have been formulated [16].

Introduction of various electron-donating or -withdrawing substituents affects the hydrogen-bonding ability of the thiourea which depends upon the acidity of thioureido –NH protons. The presence of amide group provides an additional bonding site for such studies. Fluorinated aryl thioureas represent a new class of potent anti-trypanosomal agents [17] and a novel class of potent influenza virus neuraminidase inhibitors [18]. Very recently, the in vitro antifungal activity of a series of isomeric fluoro-substituted thioureas was also determined [19].

On the other hand, the benzamido core is present in compounds with such a wide range of biological activities that it has been called a privileged structure. N-substituted benzamides are well-known anticancer compounds and the mechanism of action for N-substituted benzamide-induced apoptosis has been studied, using declopramide as a lead compound [20]. N-substituted benzamides inhibit nuclear factor-κB and nuclear factor of activated T cells activity while inducing activator protein 1 activity in T lymphocytes [21]. 2-Aminotetralin-derived substituted benzamides with mixed Dopamine D2, D3, and Serotonin 5-HT1A receptor binding properties are a novel class of potential atypical antipsychotic agents [22]. Fluoro-substituted benzamides have been also studied, suggesting the presence of strong fluorine–hydrogen short contacts and hydrogen bonds [23].

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The title compound was designed to investigate the effect of the presence of amide group as an additional bonding site in the thiourea moiety. It is unique in having both the benzamido and thiouredo moieties present in a single structural unit, which makes it an excellent model for studying their simultaneous H-bonding interactions. Here, the synthesis, characterization and vibrational properties, together with the X-ray molecular structure are reported.

## 2. Experimental

### 2.1. Synthesis

A solution of *p*-phenylenediamine (1.5 mmol) in 25 ml acetonitrile was added dropwise to a two-necked round-bottomed flask containing 4-fluorobenzoyl isothiocyanate (1.5 mmol) in 30 ml of acetonitrile. The mixture was refluxed for 3 h. On cooling, the reaction mixture was acidified with dil. hydrochloric acid. The 1-(4-aminophenyl)-3-(4-fluorobenzoyl) thiourea intermediate obtained on filtration was washed with water, died, dissolved in 30 ml of acetonitrile and treated as such with 4-fluorobenzoyl chloride (1.5 mmol) in 25 ml of acetonitrile. The reaction mixture was refluxed further for 1 h, on cooling added to water to furnish the title benzamido-thiourea (**I**) as solid. The product was recrystallized twice from ethyl acetate to afford the crystal suitable for the X-ray diffraction study (yield 87%). Anal. Calcd. for $C_{21}H_{15}F_2N_3O_2S$: C, 61.31; H, 3.67; N, 10.21; S, 7.79, Found: C, 61.24; H, 3.61; N, 10.34; S, 7.85 %. $^1H$ NMR (300 MHz, CDCl$_3$ $\delta$, ppm): 12.21 (*br s*, 1H, NH), 9.18 (*br s*, 1H, NH), 10.1 (*br s*, 1H, NH), 7.96 (*m*, 4H, Ar–H), 7.41 (*m*, 2H, Ar–H), 7.51 (*dd*, *J* = 2.7, 6.6 Hz, 2H, Ar–H), 7.41 (*m*, 2H, Ar–H), 7.09 (*dd*, *J* = 2.7, 6.6 Hz, 2H, Ar–H).

### 2.2. Crystal structure determination

$C_{23}H_{19}F_2N_3O_3S$, 0.5 ethylacetate; $M_r$ = 455.5, colorless crystal, size 0.49 × 0.33 × 0.21 mm$^3$, triclinic space group P-1, *a* = 10.1338(14), *b* = 12.7183(18), *c* = 16.930(2) Å, $\alpha$ = 85.814(3), $\beta$ = 80.934(3), $\gamma$ = 78.508(3)°, *V* = 2109.6(5) Å$^3$, *Z* = 4, $D_{calc}$ = 1.434 g/cm$^3$, *F*(0 0 0) = 944, $\mu$ = 0.202 mm$^{-1}$. Bruker SMART APEX CCD diffractometer, *T* = 120(2) K, MoKα-radiation, 15,776 intensities collected 1.6 < Θ < 26.4°, semi-empirical absorption correction from equivalents, 8333 independent reflections ($R_{int}$ = 0.052). Structure solution by direct and conventional Fourier methods, structure refinement based on $F^2$ and 578 parameters, all but hydrogen atoms refined anisotropically. H atoms were clearly resolved from $\Delta F$ maps, placed on idealized positions and refined riding on the parent atoms with $U_{iso}$ = 1.2$U_{eq}$(C or N) [24]. There are two crystallographically independent but chemically equal molecules and one ethylacetate solvent molecule per asymmetric unit. Refinement converged at $R_1$($I > 2\sigma(I)$) = 0.052, $wR_2$(all data) = 0.139, *S* = 0.933, max.($\Delta/\sigma$) = 0.001, min./max. height in final DF map −0.43/0.51 e/Å$^3$.

### 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 recorder in the region 4000–100 cm$^{-1}$ using a Bruker IFS 66v spectrometer equipped with Nd:YAG laser source operating at 1.064 μm 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 with a 19091J-433 HP-5 column, using gaseous helium as mobile phase. One peak at retention time 7.4 min is observed in the chromatogram, with a fragmentation pattern dominated by the following peaks: 123 (100%, FC$_6$H$_4$CO), 95 (60%, FC$_6$H$_4$) and 75 (28%, C$_6$H$_3$).

### 2.5. Quantum chemical calculations

All quantum chemical calculations were performed with the GAUSSIAN 03 program package [25]. The molecular geometries were optimized to standard convergence criteria by using a DFT hybrid method with Becke's non local three parameter exchange and the Lee, Young and Parr correction (B3LYP) using 6-31+G$^*$ and the more extended 6-311+G$^*$ basis sets. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found.

## 3. Results and discussion

### 3.1. Synthesis

The Synthetic pathway to 1-(4-(4-fluorobenzamido)phenyl)-3-(4-fluorobenzoyl)thiourea (**I**) is shown in Scheme 1. Thus 4-fluorobenzoyl isothiocyanate was produced *in situ*, by reaction of freshly prepared 4-fluorobenzoyl chloride with an equimolar amount of potassium thiocyanate in dry acetonitrile. Treatment of the latter with equimolar quantity of p-phenylenediamine afforded the 1-(4-aminophenyl)-3-(4-fluorobenzoyl) thiourea as an intermediate, in addition to some bis-thiourea product. Further treatment of the intermediate thiourea with another mole of 4-fluorobenzoyl chloride furnished the title compound (**I**) in 87% yield. The product was recrystallized twice from ethyl acetate to afford the crystal suitable for the X-ray diffraction study.

The $^1H$ NMR spectrum of the compound was consistent with the proposed structure. Thus, in addition to the signals for aromatic protons three N–H signals are observed. The signals appearing at $\delta$ = 12.21 ppm region and in the $\delta$ = 9.18 ppm are characteristic of the thiourea moiety. The imine group proton participating in the intramolecular hydrogen appears at low field. The N–H signal for amide appeared at $\delta$ = 10.1 ppm.

### 3.2. X-ray structure

There are two crystallographically independent molecules A (labeling 1*yz*) and B (2*yz*) per asymmetric unit that differ only slightly from their geometric parameters. Table 1 includes selected geometric parameters derived from the structure refinement, as well as those obtained from quantum chemical calculations. The fluorobenzoyl group of the thiourea moiety is twisted by about 29.2(2)° (mol. B 20.6(2)°) along the Cx01–Cx02 bond from the thiourea plane. The fluorobezamido phenyl part as well is twisted, both aromatic subunits define a dihedral angle of 15.0(1)° (mol. B 18.3(1)°). Thiourea (Cx01, Ox01, Nx01, Cx08, Sx01, Nx02) and amido planes (Nx03, Cx15, Ox02) are also twisted by 34.8(1)° (mol. B 26.5(1)°) (see Fig. 1).

The structure of substituted thioureas generally shows a significant influence of intramolecular hydrogen bonding, which results in substancial differences between the preferred conformation of the *N,N* di-substituted molecules, compared with the *N*-substituted analogue [26]. Koch and co-workers [13,27] and Dago et al. [6] reported that an intramolecular hydrogen bond between the thiourea group and the oxygen atom of the amidic group stabilizes a planar six member ring structure. Following this trend, in the title molecule the –C(O)NHC(S)NH– unit adopt a planar structure with the C=O group interacting with the $N_{102}$–H amidic group in a similar manner. The nonbonding distance $O_{101}\cdots N_{102}$ is 2.635(2) Å,
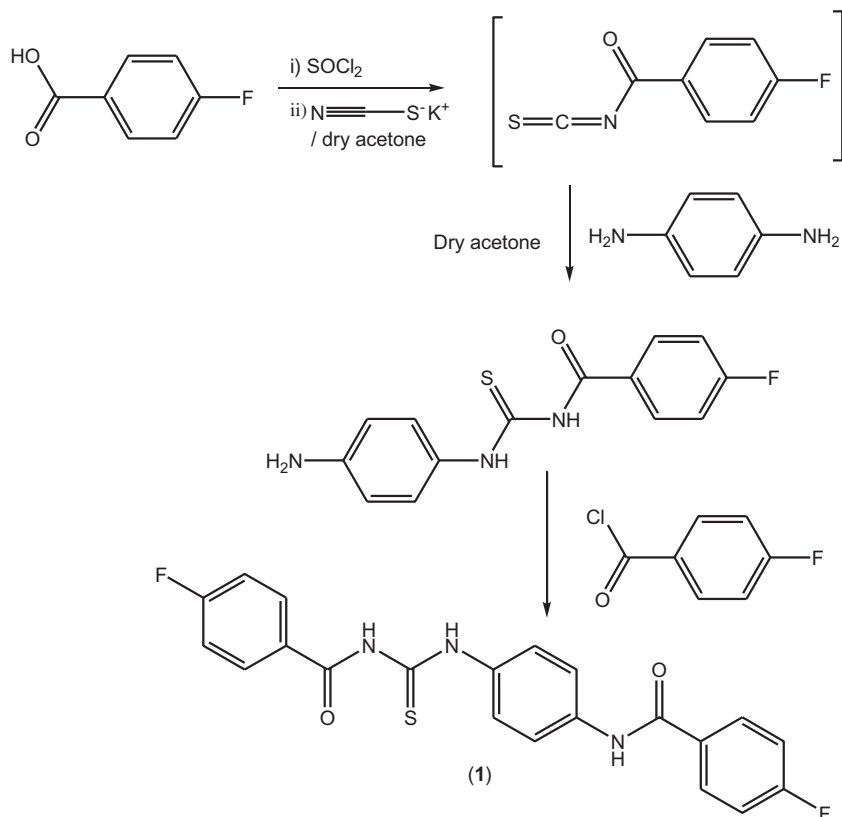
**Scheme 1.** Synthetic pathway to 1-(4-(4-Fluorobenzamido)phenyl)-3-(4-fluorobenzoyl) thiourea.

**Table 1**
Experimental and calculated selected geometric parameters (values in Å and degrees) for the title species.

|  | Experimental | B3LYP/6-311+G* |
|---|---|---|
| *Bond lengths* | | |
| $C_{101}=O_{101}$ | 1.225(3) | 1.228 |
| $C_{115}=O_{102}$ | 1.226(3) | 1.221 |
| $C=S$ | 1.654(2) | 1.674 |
| $C_{101}-N_{101}$ | 1.374(3) | 1.380 |
| $N_{103}-C_{115}$ | 1.347(3) | 1.378 |
| $N_{102}-C_{108}$ | 1.323(3) | 1.345 |
| $N_{101}-C_{108}$ | 1.400(3) | 1.415 |
| *Bond angles* | | |
| $O_{101}=C_{101}-N_{101}$ | 123.1(2) | 122.7 |
| $C_{101}-N_{101}-C_{108}$ | 127.7(2) | 130.4 |
| $N_{101}-C_{108}-S_{101}$ | 117.91(18) | 116.3 |
| $N_{102}-C_{108}-S_{101}$ | 126.48(18) | 129.7 |
| $N_{103}-C_{115}=O_{102}$ | 123.3(2) | 123.7 |
| $N_{103}-C_{115}-C_{116}$ | 115.3(2) | 114.9 |
| *Dihedral angles* | | |
| $O_{101}-C_{101}-N_{101}-C_{108}$ | 7.2(4) | −4.4 |
| $C_{101}-N_{101}-C_{108}-N_{102}$ | 1.8(4) | 1.2 |
| $C_{108}-N_{102}-C_{109}-C_{110}$ | −3.3(4) | −1.8 |
| $O_{102}-C_{115}-N_{103}-C_{112}$ | −0.8(4) | −2.4 |
| $C_{113}-C_{112}-N_{103}-C_{115}$ | 41.4(4) | −6.2 |
| $O_{102}=C_{115}-C_{116}-C_{121}$ | −24.2(3) | −26.3 |
| $C_{103}-C_{102}-C_{101}=O_{101}$ | 27.8(4) | −20.9 |

similar to that found in other *N*-benzoyl *Ń*-substituted thioureas, which are reported in the range of 2.618(4)–2.654(2) Å [3,28].

Table 1 shows the carbon–nitrogen bond lengths determined for the central –C(O)NHC(S)NH– moiety. It is observed that both the amidic [(O)$C_{101}-N_{101}$ 1.374(3) Å] and thioamide [$N_{102}-C_{108}$(S) 1.323(3) Å] bonds have a partial double bond character. Moreover, a definite trend in the C–N bond distances has been recognized for

these species [26], the lengths increasing in the order $C_{108}-N_{102} < C_{101}-N_{101} < C_{108}-N_{101}$ (see Table 1). For comparison, the corresponding C–N bond length in the benzoyl amide group ($C_{115}-N_{103}$) amounts 1.347(3) Å, slightly shorter than the $C_{101}-N_{101}$ bond.

The patterns of packing adopted by thiourea derivatives were rationalized by McBride et al. in terms of molecular structure, solvent of crystallization, and energies and efficiencies of packing [29]. For the title species, the crystal packing is dominated by intermolecular $N_{101}-H\cdots S=C$ (−x, −y, −z + 1) and $N_{201}-H\cdots S_{201}=C$ (−x + 1, −y, −z + 1) hydrogen bonds [2.546(1) Å] connect molecules into centrosymmetric dimers that are stacked in parallel sheets along the [1 0 0] plane. This is a well-known crystal motif for *N*-benzoyl-thiourea compounds [5,30]. The presence of ethyl acetate molecules in the crystal seems to play a minor role in the X-ray molecular structure and crystal packing. It was reported that the crystallization of bis(thiourea) derivatives containing the 1,3-dimetrhyl-adamantane linker from ethyl acetate affords crystals containing disordered solvent molecules [31]. In the present case, the main interaction is given by $C=O\cdots H-N_{103}$ hydrogen bonds [3.311(1) Å] involving the carbonyl ester group of the solvent molecule and the amide group of the title species.

### 3.3. Quantum chemical calculations

The molecular structure and conformational flexibility are important properties for determining the donor–acceptor capabilities on thiourea derivatives [32,33]. Fabbrizzi et al. reported that substituted-phenyl urea compounds interacts through hydrogen bonding with a variety of oxoanions to give bright colored complexes [34] and a variety of receptors containing the urea and the thiourea groups were designed for anion recognition [35]. These effects are closely related with the conformational
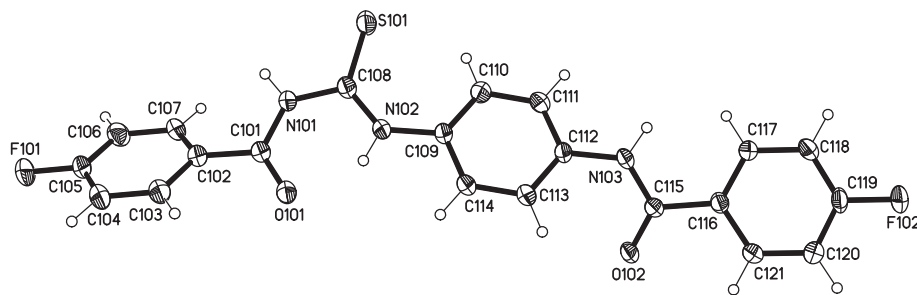
**Fig. 1.** Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Only one molecule (A) present in the asymmetric unit is shown, the second molecule (B) follows labeling scheme with 2xx.

properties and the presence of intra- and intermolecular hydrogen bonding interactions on the thiourea group [35].

Thus, the conformational space and the molecular structures for the main conformations of the studied compound have been analyzed by using quantum chemical calculations at the DFT-B3LYP level of approximation. The comparison between experimental X-ray results with the corresponding computed structure for the molecule isolated in a vacuum allows for a better understanding of the conformational transferability observed for substituted thioureas. In principle, the studied compounds may adopts several conformations mainly depending on the orientation around the thiourea moiety, the relative position of the C=O and C=S double bonds and the orientation of substituted-phenyl rings. Thus, in order to define the conformational flexibility of the title molecule, in a first approximation the potential energy functions for internal rotation around the dihedral angles of the central –C(O)NHC(S)NH– group have been calculated. The B3LYP method with the moderate 6-31G basis sets has been applied allowing geometry optimizations with the corresponding dihedral angle varying from 0° to 360° in steps of 20°. The potential energy curves obtained around the $N_{101}$–$C_{108}$ and $C_{101}$–$N_{101}$ single bonds are shown in Fig. 2.

The potential energy curve for the rotation around the $N_{101}$–$C_{108}$ bond in the thiourea moiety (Fig. 2, left) shows a deep minimum at $\delta(CN_{101}$–$C_{108}$=S) = 180°, corresponding to a structure with the thiourea group adopting a planar form with the C=S double bond and the $N_{101}$–$C_{101}$ bond in mutual anti conformation. The syn form [$\delta(CN_{101}$–$C_{108}$=S) = 0°] is located in a local maximum,

probably corresponding to a transition state structure. When the second dihedral angle involving the thiourea group [$\delta(O$=$C_{101}$–$N_{101}C)$] is studied the potential energy curve shows the presence of a well-defined minimum at $\delta(O$=$C_{101}$–$N_{101}C)$ = 0°, corresponding to the expected planar synperiplanar orientation of the C=O double bond with the $N_{101}$–$C_{108}$ bond. The curve is symmetrical with respect to the antiperiplanar orientation $\delta(O$=$C_{101}$–$N_{101}C)$ = 180°, which seems to be located in a local maximum of the potential curve, higher in energy by ca. 14 kcal mol$^{-1}$. It is worthy to note that in the most stable form, the C=O and C=S double bonds are mutually oriented in opposite directions. Additionally, the $N_{101}$–H and $N_{102}$–H bonds in the thiourea group adopt a syn and anti conformation with respect to the C=S double bond, respectively.

Also, full geometry optimizations and frequency calculations were computed for each of the more stable structures with the B3LYP method and the 6-31+G* basis sets. The optimized molecular structures for the two main conformers of the studied compound are shown in Fig. 3. The corresponding conformer analogous to those found in the X-ray analysis was further optimized by using the more extended triple-zeta 6-311+G* basis sets and selected computed geometrical parameters are gathered in Table 1. The geometrical parameters obtained at the B3LYP/6-311+G* are in very good agreement with the experimental ones.

Of particular interest, the $C_{108}$–$N_{101}$ bond length is computed as the longest nitrogen–carbon bond in the molecule, in fine agreement with the structure determined by X-ray diffraction. Thus, it is quite likely that intramolecular electronic effects (especially res-
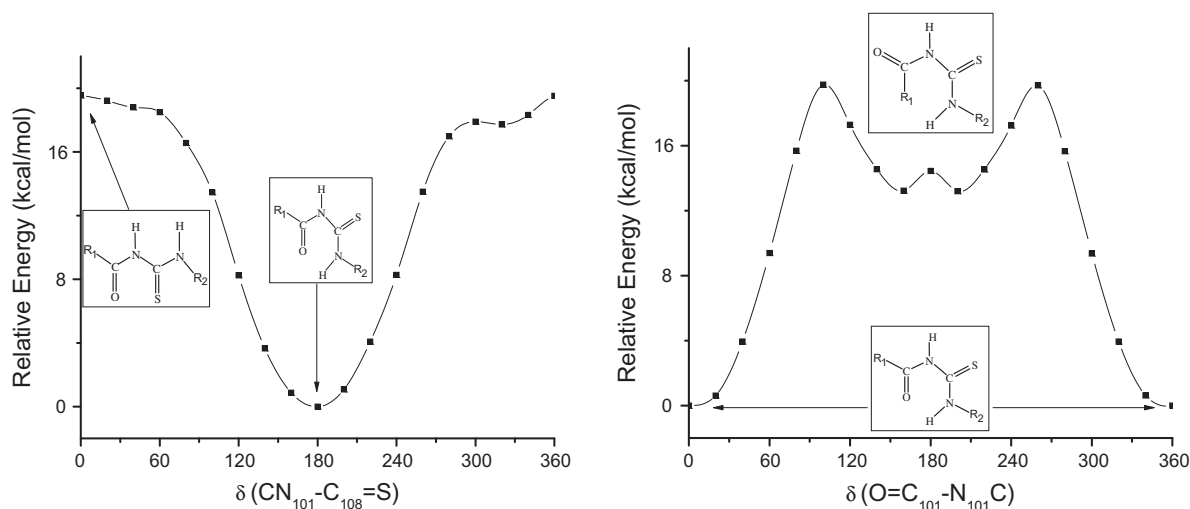


**Fig. 2.** Calculated (B3LYP/6-31G) potential energy function for internal rotation around the $N_{101}$–$C_{108}$ (left) and $C_{101}$–$N_{101}$ (right) single bonds in the central –C(O)NHC(S)NH– moiety (for atom numbering see Fig. 1). The molecular schemes have been inserted for better visualization of the conformational space ($R_1$ = $C_6H_4F$– and $R_2$ = $C_6H_4$–NHC(O)–$C_6H_4F$).
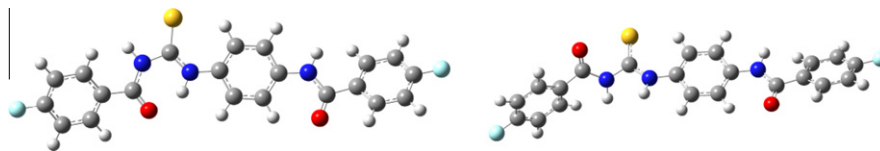
**Fig. 3.** Molecular models for the main conformers of the title species found theoretically (B3LYP/6-31+G*). In the most stable conformer (left) the C=S and C=O bond are oriented in opposite directions.

onance interactions) rather than crystal packing effects dominate the trend observed for the N–C bond lengths.

Finally, it is worthy to mention that a strong intramolecular hydrogen bond between the C=O and H–$N_{102}$ groups seems to be favored in the most stable form also in the vacuum isolated species. This interaction forms a 6-membered ring, with $N_{101}$ and $C_{108}$, and a short non-bonded contact of ca. 2.692 Å is computed (B3LYP/6-311+G*) for the $C=O_{101}\cdots N_{102}$ distance, in very good agreement with the observed value in the crystal structure.

### 3.4. Vibrational analysis

The observed and calculated (B3LYP/6-311+G*) infrared absorptions, the FT-Raman frequencies along with their relative intensities and probable assignments are summarized in Table S1, in the supporting information. A tentative assignment of the observed bands has been carried out by comparison with the spectra of related molecules [27,36–41]. Very recently, the vibrational properties of the thiourea molecule – the idealized parent species – were revisited by Srinivasan et al. [42].

In the infrared spectra a series of broad absorptions of medium intensity are observed at 3286, 3190 and 2923 cm$^{-1}$, which could be assigned to the N–H stretching modes [40,43,44]. The most intense of these band at 2923 cm$^{-1}$ could be tentatively assigned to the $v(N102-H)$ stretching mode. Weiqun et al. [2] also reported a low $v(N-H)$ frequency value (3086 cm$^{-1}$) for the related N-(4-chloro)benzoyl-Ń(4-tolyl)thiourea species. Quantum chemical calculations for the most stable conformer of the title compound isolated in a vacuum compute that the $v(N102-H)$ stretching mode appears as a very intense absorption at 3384 cm$^{-1}$ (not corrected), shifted to lower frequencies as compared with both the $v(N102-H)$ and $v(N103-H)$ fundamentals (3621 cm$^{-1}$). This red-shift observed for the $v(N-H)$ stretching mode could be related with the formation of C=O$\cdots$N–H intramolecular hydrogen bond, as observed in the X-ray analysis. Interestingly, the computed vibrational spectrum for the second stable conformer – for which intramolecular hydrogen bonds are not expected – shows the presence of three absorptions with similar intensity at 3613, 3579 and 3572 cm$^{-1}$.

Strong IR absorptions at 1674 and 1645 cm$^{-1}$ were assigned to the $v(C=O)$ modes, frequency values which are similar to that found in many small-molecule having C=O$\cdots$H–N hydrogen bonding [45]. The respective Raman bands are observed at 1672 and 1644 cm$^{-1}$, respectively. Calculated (B3LYP/6-311+G*) frequencies for these fundamentals amount 1731 and 1720 cm$^{-1}$ for the $v(C_{115}=O_{102})$ and $v(C_{101}=O_{101})$ stretching modes, respectively. The lower value computed for the –C(O)NHC(S)NH– carbonyl as compared with the amidic group is in accordance with the presence of a intramolecular C=O$\cdots$H–N interaction in the –C(O)NHC(S)NH– moiety. These facts are in agreement with the comprehensive vibrational study of Reguera et al. for substituted thioureas displaying intramolecular hydrogen bonding [46]. 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 [47–49]. Moreover, the relative low frequency values observed for the $v(C=O)$ stretching mode in N-benzoyl substituted thiourea compounds has been also interpreted as

being a result of conjugated resonance interactions between the carbonyl and the phenyl ring [2].

It is well-known that both the amide and thiourea groups present a characteristic 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, strong IR absorptions with defined maxima at ca. 1603 and 1526 cm$^{-1}$, are assigned to these modes. The most intense Raman signal is located in this region at 1607 cm$^{-1}$. B3YLP/6-311+G* computations predict a strong band due to the $\delta$(N102–H) normal mode at 1666 cm$^{-1}$, whereas the $\delta$(N103–H) and $\delta$(N101–H) are predicted at lower frequencies (1646 and 1622 cm$^{-1}$, respectively).

In relation to the spectroscopic peculiarities of phenyl groups, characteristic group frequencies are observed. A series of absorptions in the 1620–1500 cm$^{-1}$ range, with a strong band at 1511 cm$^{-1}$, are mainly originated in the several C–C stretching vibrations of the benzene and substituted fluorobenzyl rings of the molecule [48].

Strong bands can be observed at 1360 and 1329 cm$^{-1}$ in the Raman spectrum of the studied compound, with strong counterparts at 1352 and 1329 cm$^{-1}$ in the infrared spectrum. Taking into account the vibrational properties reported for the simple thiourea molecule [42], it is expected that the C–N stretching modes, which are usually coupled in symmetric and antisymmetric motions, appear in this region [47]. Thus, following the quantum chemical calculation description of these normal modes, the NCN antisymmetric stretching mode of the thiourea moiety is assigned to the intense band centered at 1352 cm$^{-1}$. The computed value at the B3LYP/6-311+G* level of approximation is 1398 cm$^{-1}$ and corresponds to the most intense absorption, in good agreement with the experimental evidence.

The $v(C-F)$ stretching modes originate medium intensity infrared absorptions at 1258 and 1231 cm$^{-1}$, with counterparts at 1262 cm$^{-1}$ and 1233 cm$^{-1}$ in the Raman spectrum, respectively.

The medium intensity IR absorption observed at 756 cm$^{-1}$ is tentatively assigned to the $v(C=S)$ mode. This assignment is in agreement with previously studied thiourea derivatives [3,46]. However, it should be mentioned that for the parent the thiourea molecule, this mode appeared in the 1094 cm$^{-1}$ in the infrared spectrum (1105 cm$^{-1}$ Raman) [42], and higher values – up to 1325 cm$^{-1}$ – have been also reported [2,38]. The formation of C=S$\cdots$H–X intermolecular hydrogen bonds seems to strongly affect the frequency of the $v(C=S)$ mode [36].

## 4. Conclusion

The title compound having benzamido and thiourea moieties in a single structural unit has been synthesized and characterized by spectroscopic and X-ray diffraction techniques. The presence of amide carbonyl group provides an additional bonding site in addition to the thioureido carbonyl and thiocarbonyls, thus increasing its bonding potential as a versatile ligand for coordination to metals. DFT methods have been used to determine the conformational space around the central –C(O)NHC(S)NH– moiety and the vibrational properties have been studied by FTIR and FT-Raman spectroscopies along with quantum chemical calculations at the B3LYP/6-311+G*. A strong intramolecular hydrogen bond between

the C=O and H–N$_{102}$ groups forming a 6-membered ring seems to be favored in the most stable form in both the crystal and in the vacuum isolated species.

## Acknowledgments

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.09.035.

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