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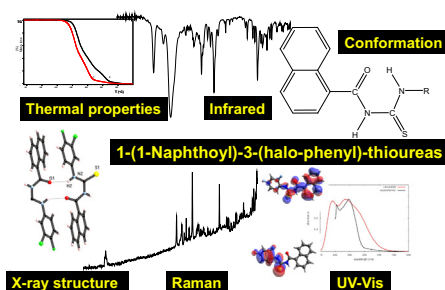
## Synthesis, X-ray crystal structure, thermal behavior and spectroscopic analysis of 1-(1-naphthoyl)-3-(halo-phenyl)-thioureas complemented with quantum chemical calculations

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### HIGHLIGHTS

- Crystal structures and thermal properties were determined for 1-naphthoyl thioureas.
- The C=O and C=S double bonds of the acyl-thiourea group are mutually oriented in opposite directions.
- Strong N–H···O=C intramolecular hydrogen bond determined the conformational properties.
- Intermolecular N–H···S=C and N–H···O=C hydrogen bonds are observed.
- Vibrational and UV–Vis spectra are assigned.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Two novel 1-(1-naphthoyl)-3-(halo-phenyl) substituted thioureas, namely 1-(1-naphthoyl)-3-(2,4-di-fluoro-phenyl)-thiourea (**1**) and 1-(1-naphthoyl)-3-(3-chloro-4-fluoro-phenyl)-thiourea (**2**), were synthesized and fully characterized. The X-ray crystal and molecular structures have been determined resulting in a planar acylthiourea group, with the C=O and C=S adopting a pseudo-antiperiplanar conformation. An intramolecular N–H···O=C hydrogen bond occurs between the thioamide and carbonyl groups. The crystal packing of both compounds is characterized by extended intermolecular N–H···S=C and N–H···O=C hydrogen-bonding interactions involving the acylthiourea moiety. Compound **2** is further stabilized by  $\pi$ -stacking between adjacent naphthalene and phenyl rings. The thermal behavior, as well as the vibrational properties, studied by infrared and Raman spectroscopy data complemented by quantum chemical calculations at the B3PW91/6-311++G(d,p) support the formation of these intra- and intermolecular hydrogen bonds. Furthermore, the UV–Vis spectrum is interpreted in terms of TD-DFT quantum chemical calculations with the shapes of the simulated absorption spectra in good accordance with the experimental data.

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### Introduction

Increasing attention is devoted to the structural and conformational elucidation of 1-(acyl/aryl)-3-(mono-substituted) thiourea derivatives since these properties mostly determine the behavior

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of these compounds as ionophores for ion selective electrodes [1–4] and chemosensors for naked-eye recognition of anions [5–8]. In particular, the thiourea molecule and the acceptor anion participate in hydrogen bond interactions [9], playing also an important role in terms of biological activity displayed by these compounds [10]. It is well-documented [11] that a local planar structure of the  $-C(O)NHC(S)NH-$  moiety is preferred for 1-(acyl/aroil)-3-(mono-substituted) thiourea, with opposite orientation between the  $C=O$  and  $C=S$  double bonds (“S-shape”) [12]. A pseudo six-membered ring is formed in this conformation, associated with the promotion of a  $C=O \cdots H-N$  intramolecular hydrogen bond [13].

Several reports on 1-acyl-3-naphthyl substituted thiourea derivatives can be found in the literature [14–19]. Less attention, however, has been received by the isomeric 1-(naphthoyl)-3-substituted thiourea compounds (see Scheme 1). A series of 1-(naphthoyl)-3-mono substituted and 3,3-di-substituted thioureas were synthesized by Dzurilla et al. [20] and their behavior toward the oxidation with  $Br_2$  in chloroform (Hugershoff reaction) was determined. The capabilities of (1-naphthyl)-arylamidine compounds as ligand were investigated and their  $Cu^{II}$ -,  $Ni^{II}$ - and  $Pd^{II}$ -complexes have been prepared [21]. In these complexes, the anionic O,S bis-chelate coordination mode was found and near-square-planar geometries around the central metal with a *cis* arrangement was determined [21]. Di-thiourea derivatives substituted by 2-naphthoyl groups were also structurally characterized [22].

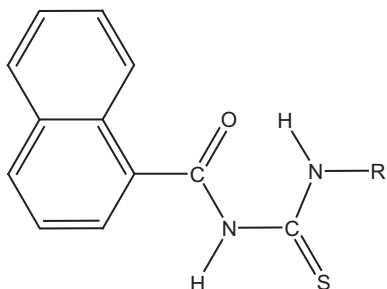
Continuing our ongoing project aimed to the synthesis of 1-(acyl/aroil)-3-(mono-substituted) thioureas [23,24], here we report the preparation and spectroscopic characterization of two closely related thioureas having the 1-(1-naphthoyl) group and 3-(2,4-di-fluoro-phenyl) (**1**) and 3-(3-chloro-4-fluoro-phenyl) (**2**) substitution. The crystal structures have been determined by single-crystal X-ray diffraction. Their NMR, mass spectra, infrared and Raman and UV-Vis spectroscopic properties were also discussed. The assignment of the bands was accomplished with the aid of quantum chemical calculations. The thermogravimetric studies were analyzed.

## Experimental

### Instrumentation

Melting points were recorded using a digital Gallenkamp (SANYO) model MPD.BM 3.5 apparatus and are uncorrected.  $^1H$  NMR and  $^{13}C$  NMR spectra were determined in DMSO-d solution at 300 and 75.5 MHz respectively using a Bruker AM-300 spectrophotometer. Mass Spectra (EI, 70 eV) were taken on a GC-MS, Agilent technologies 6890 N with an inert mass selective detector 5973 mass spectrometer and elemental analyses were conducted using a LECO-183 CHNS analyzer.

Fourier transform infrared spectroscopy (FTIR), spectra were recorded on an FTS 3000 MX spectrophotometer (Pakistan).



**Scheme 1.** Representation of the *S* conformer in 1-(1-naphthoyl)-3-(mono) substituted thioureas.

Infrared spectra were recorded in KBr pellets with a resolution of  $2\text{ cm}^{-1}$  in the  $4000\text{--}400\text{ cm}^{-1}$  range on a Bruker EQUINOX 55 FTIR spectrometer (Argentina). The FT-Raman spectra were recorded in the region  $4000\text{--}100\text{ cm}^{-1}$  using a Bruker IFS 66v spectrometer equipped with Nd:YAG laser source operating at  $1.064\text{ }\mu\text{m}$  line with  $200\text{ mW}$  power of spectral width  $2\text{ cm}^{-1}$ . UV-Vis spectra in DMSO solution were recorded using a standard quartz cell placed in the sample compartment of a UV-Vis Hewlett-Packard 8454-A diode array spectrometer ( $2\text{ nm}$  resolution).

Thermal analyses were performed with Shimadzu TGA-50 unit, between room temperature and  $500\text{ }^\circ\text{C}$ , at a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$  and nitrogen flow of  $50\text{ ml}/\text{min}$ .

### Quantum chemical calculations

Optimization of both structure geometries was accomplished within the frame work of the density functional theory [25,26] using the hybrid functional with non-local exchange due to Becke [27] and the correlation functional due to Perdew and Wang [28], known as B3PW91 as implemented in the Gaussian 03 package [29]. Contracted gaussian basis sets of triple-zeta quality plus polarized and diffuse functions 6-311++G(d,p) for all atoms were used throughout the present work [30]. The corresponding vibrational analyses were performed for the optimized geometries to verify whether they are local minima or saddle points on the potential energy surface of the molecule. Calculated normal modes were also used as an aid in the assignment of experimental frequencies. Scale factors were used along the present work [31]. The computed Raman activities ( $S_i$ ) were converted to relative Raman intensities ( $I_i$ ) using the following relationship [32]:

$$I_i = f(v_0 - \nu_i)4S_i/\nu_i[1 - \exp(-h\nu_i/kT)]$$

where  $\nu_0$  is the exciting wavenumber (in  $\text{cm}^{-1}$  units);  $\nu_i$  is the vibrational wave number of the *i*th normal mode;  $h$ ,  $c$  and  $k$  are the universal constants; and  $f$  is the suitably chosen common scaling factor for all the peak intensities.

The Potential Energy Distribution PED analysis are computed from the B3LYP/6-311++G(d,p) calculated vibrational frequencies using VEDA4 program [33,34].

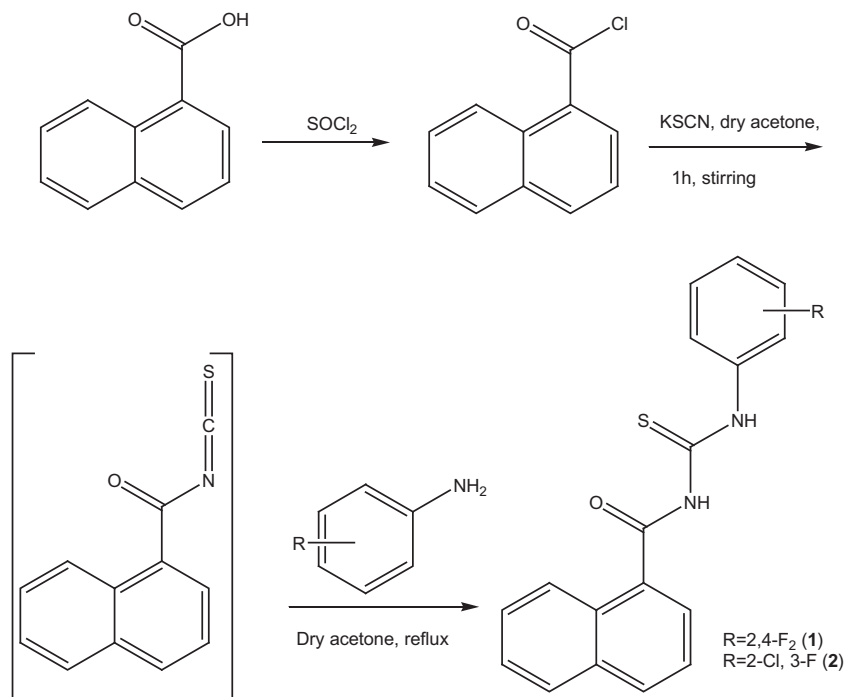
The vertical transition energies were calculated at the optimized ground-state geometry using the time-dependent density functional theory [35] at the same level of theory used for optimization a vibrational calculations taking into account solvent effects (DMSO) through the Polarizable Continuum Model [36] to produce a number of 20 singlet-to-singlet transitions.

### Crystallography

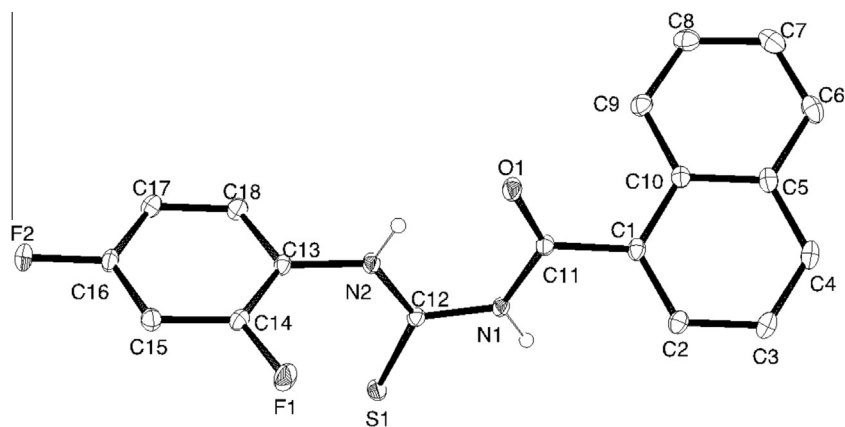
Intensity data were collected on a Oxford SuperNova CCD diffractometer using Mo-K $\alpha$  radiation (graphite crystal monochromator  $\lambda = 0.71073\text{ \AA}$ ). The temperature during both data collections was maintained at  $130.0(1)$ .

**Crystal data for 1:**  $C_{18}H_{12}F_2N_2OS$ ,  $M = 342.36$ ,  $T = 130.0(2)\text{ K}$ ,  $\lambda = 0.7107\text{ \AA}$ , Monoclinic, space group  $P21/n$   $a = 10.8284(3)$ ,  $b = 6.85394(16)$ ,  $c = 21.2605(5)\text{ \AA}$ ,  $\beta = 104.554(2)^\circ$ ,  $V = 1527.26(6)\text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.489\text{ Mg M}^{-3}$   $\mu(\text{Mo-K}\alpha) = 0.241\text{ mm}^{-1}$ ,  $F(000) = 704$ , crystal size  $0.67 \times 0.49 \times 0.24\text{ mm}$ .  $\theta_{\text{max}} = 32.28^\circ$ , 17,375 reflections measured, 4995 independent reflections ( $R_{\text{int}} = 0.029$ ) the final  $R = 0.0384$  [ $I > 2\sigma(I)$ , 4149 data] and  $wR(F^2) = 0.0995$  (all data)  $\text{GOOF} = 1.045$ .  $\text{CCDC } 896972$ .

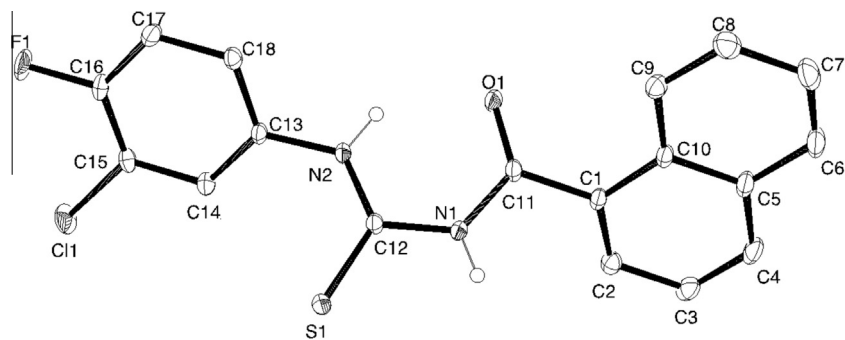
**Crystal data for 2:**  $C_{18}H_{12}ClFN_2OS$ ,  $M = 358.81$ ,  $T = 130.0(2)\text{ K}$ ,  $\lambda = 0.7107\text{ \AA}$ , Triclinic, space group  $P-1$   $a = 7.3692(3)$ ,  $b = 7.4216(3)$ ,  $c = 15.4693(7)\text{ \AA}$ ,  $\alpha = 81.896(4)^\circ$ ,  $\beta = 76.505(4)^\circ$ ,  $\gamma = 88.369(3)^\circ$   $V = 814.45(6)\text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.463\text{ Mg M}^{-3}$   $\mu(\text{Mo-K}\alpha) = 0.380\text{ mm}^{-1}$ ,  $F(000) = 368$ , crystal size  $0.50 \times 0.36 \times 0.05\text{ mm}$ .  $\theta_{\text{max}} = 32.17^\circ$ , 9709 reflections measured, 5165



**Scheme 2.** Synthetic route to 1-(1-naphthoyl)-3-(halo-phenyl)-thioureas.



**Fig. 1.** Molecular structure of compound 1 in a single crystal at 130 K (with the thermal ellipsoids shown at a 30% probability level).



**Fig. 2.** Molecular structure of compound 2 in a single crystal at 130 K (with the thermal ellipsoids shown at a 30% probability level).

**Table 1**Bond lengths (Å) and angles (°) observed and calculated for the central thiourea moiety for **1** and **2**.

Compound	<b>1</b>		<b>2</b>	
	Experimental	Calculated	Experimental	Calculated
<i>Bond distances</i>				
C12=S1	1.669(1)	1.666	1.671(2)	1.663
C11=O1	1.230(2)	1.225	1.225(2)	1.227
N1—C11	1.380(1)	1.380	1.382(2)	1.378
N1—C12	1.394(2)	1.404	1.394(2)	1.407
N2—C12	1.333(2)	1.346	1.332(2)	1.345
N2—C13	1.425(2)	1.423	1.426(2)	1.410
<i>Bond angles</i>				
N2C=S1	123.9(2)	129.5	125.4(1)	129.7
N2C12N1	116.1(1)	113.8	116.2(1)	113.4
N1C=S1	119.98(9)	116.6	118.4(1)	116.9
N1C11=O1	122.7(1)	122.3	122.7(1)	122.4
<i>Dihedral angles</i>				
S1=C12—N1C11	176.1(2)	178.7	168.6(2)	178.6
O1=C11—C1C10	48.4(6)	40.5	49.0(5)	40.5

independent reflections ( $R_{\text{int}} = 0.024$ ) the final  $R = 0.0433$  [ $I > 2\sigma(I)$ , 4104 data] and  $wR(F^2) = 0.1124$  (all data) GOOF = 1.046. CCDC 896970.

#### Synthesis of 1-(1-naphthoyl)-3-(halo-phenyl)-thioureas: general procedure

Naphthalene-1-carboxylic acid, anilines and thionyl chloride were purchased from Aldrich. Analytical grade acetone (E. Merck) was dried and freshly distilled prior to use. Naphthalene-1-carboxylic acid (1 mmol) was placed in a 100 ml two neck round bottom flask, fitted with a reflux condenser and a gas trap. Thionyl chloride (1.2 mol) followed by two drops wise addition of dry DMF and the reaction mixture was heated under reflux for 3 h to give the acid chloride. To a stirred solution of potassium thiocyanate (1 mmol) in 20 ml dry acetone, placed in a 250 ml two necked round bottom flask fitted with a reflux condenser, freshly prepared 1-naphthoyl chloride (1 mmol) was added dropwise and the mixture was refluxed for 30 min. After the initial reaction has subsided, a solution of suitably substituted aniline (1 mmol) in 20 ml dry acetone was added slowly and the resulting mixture was stirred during 1–2 h under reflux. The progress of the reaction was monitored by thin layer chromatography. After the completion, the reaction mixture was poured into crushed ice. The thiourea formed was precipitated as a solid which was then filtered off, washed well with cold distilled water, dried and recrystallized from ethanol to afford thioureas **1** and **2**.

#### 1-(1-Naphthoyl)-3-(2,4-difluoro-phenyl)-thiourea (**1**)

Light yellow crystals; Yield: 75%;  $R_f$ : 0.54; m.p: 187 °C; IR (neat,  $\text{cm}^{-1}$ ): 3169 (m,  $\nu\text{N-H}$ ), 1679 (s,  $\nu\text{C=O}$ ), 1535 (vs  $\delta\text{NH}$ ), 1279 (vs  $\nu\text{CNC}$ ).  $^1\text{H-NMR}$  ( $(\text{CD}_3)_2\text{SO}$ , 300 MHz):  $\delta$  12.43 (s, 1H, NH), 12.22 (s, 1H, NH), 8.23 (d, 1H,  $J = 8.0$ , Ar-H), 8.13 (d, 1H,  $J = 8.1$ , Ar-H), 8.06–7.98 (m, 2H, Ar-H), 7.85 (d, 1H,  $J = 7.0$ , Ar-H), 7.68–7.58 (m, 3H, Ar-H), 7.43–7.36 (m, 1H, Ar-H), 7.19–7.13 (m, 1H, Ar-H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 75.5 MHz):  $\delta$  182.5 (C=S), 171.4 (C=O), 162.4 (d,  $^3J = 12$  Hz, ArC), 159.2 (d,  $^3J = 12$  Hz, ArC), 158.0 (d,  $^3J = 12.0$  Hz, ArC), 154.7 (d,  $^3J = 12.8$  Hz, ArC), 133.4, 132.1, 131.5, 130.0, 129.3 (d,  $^3J = 9.8$  Hz, ArC), 128.9, 127.8 (d,  $^3J = 10.5$  Hz, ArC), 126.9, 125.1, 123.4 (dd,  $J = 3.8$ , 11.3 Hz, ArC), 111.6 (dd,  $J = 3.8$ , 22.6 Hz, ArC), 104.8 (dd,  $J = 24.2$ , 27.2 Hz, ArC), 79.4. Anal. Calcd. For  $\text{C}_{18}\text{H}_{12}\text{F}_2\text{N}_2\text{OS}$ , C, 63.15; H, 3.53; N, 8.18; S, 9.36%; Found: 62.97; H, 3.57; N, 8.21; S, 9.41%. GCMS ( $m/z$ ): 342 ( $\text{M}^+$ , 1%), 127 ( $\text{C}_{10}\text{H}_7^+$ , 100%), 155 ( $\text{C}_{10}\text{H}_7\text{CO}^+$ , 95%), 213 ( $\text{C}_{10}\text{H}_7\text{CONCS}^+$ , 10%).

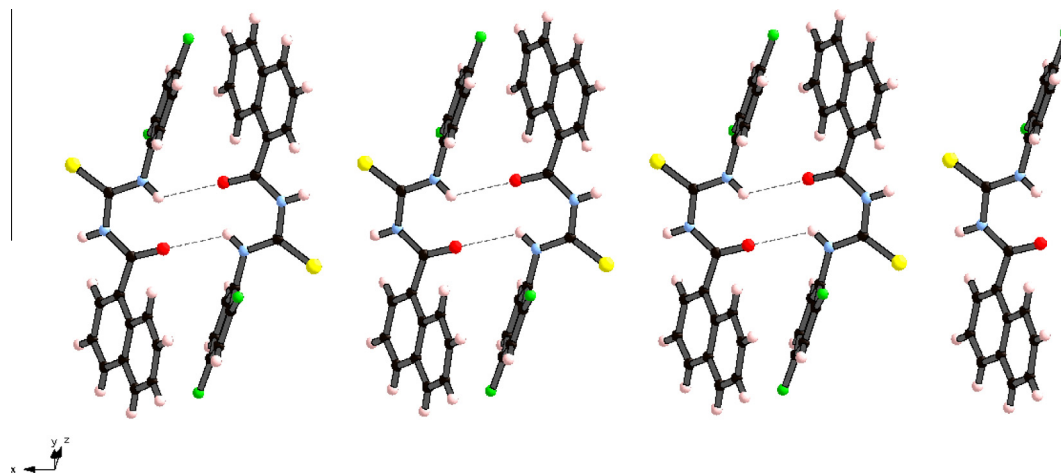
#### 1-(1-Naphthoyl)-3-(3-chloro-4-fluoro-phenyl)-thiourea (**2**)

Light yellow solid; Yield: 91%;  $R_f$ : 0.56; m.p: 195 °C; IR (neat,  $\text{cm}^{-1}$ ): 3219 (m,  $\nu\text{N-H}$ ), 1680 (s,  $\nu\text{C=O}$ ), 1534 (vs  $\delta\text{NH}$ ), 1268 (vs  $\nu\text{CNC}$ ).  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 300 MHz):  $\delta$  12.65 (s, 1H, NH), 12.03 (s, 1H, NH), 8.23 (d, 1H,  $J = 8.3$ , Ar-H), 8.13 (d, 1H,  $J = 8.0$ , Ar-H), 8.05–8.02 (m, 1H, Ar-H), 7.83–7.79 (m, 2H, Ar-H), 7.67–7.58 (m, 3H, Ar-H), 7.42–7.31 (m, 2H, Ar-H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 75.5 MHz):  $\delta$  179.6, 170.4, 162.19 (d,  $^1J = 243.0$  Hz, ArC), 140.1 (d,  $^3J = 10.6$  Hz, ArC), 133.4, 132.1, 131.7, 130.6 (d,  $^3J = 9.0$  Hz, ArC), 130.0, 128.9, 127.7 (d,  $^3J = 17$  Hz, ArC), 126.9, 125.2, 120.7, 113.5, 113.3, 111.7, 111.4. Anal. Calcd. For  $\text{C}_{18}\text{H}_{12}\text{FCIN}_2\text{OS}$ , C, 60.25; H, 3.37; N, 7.81; S, 8.93%; Found: C, 60.19; H, 3.42; N, 7.79; S, 8.94%. GCMS ( $m/z$ ): 127 ( $\text{C}_{10}\text{H}_7^+$ , 100%), 155 ( $\text{C}_{10}\text{H}_7\text{CO}^+$ , 90%), 213 ( $\text{C}_{10}\text{H}_7\text{CONCS}^+$ , 10%), 77 (15%).

## Results and discussion

### Synthesis and characterization

The synthetic pathway is shown in the [Scheme 2](#). 1-Naphthoyl chloride was freshly prepared from the commercial 1-naphthoic acid according to the standard procedure [37] and added to a solution of potassium thiocyanate in dry acetone to obtain the 1-naphthoyl isothiocyanate as an intermediate via stirring at room temperature followed by the reflux. The latter was separately reacted with 2,4-difluoro- and 3-chloro-4-fluoro-anilines to afford the corresponding thioureas as crude solids. Re-crystallization



**Fig. 3.** Partial packing diagram for compound **1** showing the H-bonded chains extending along the x direction in the crystal.

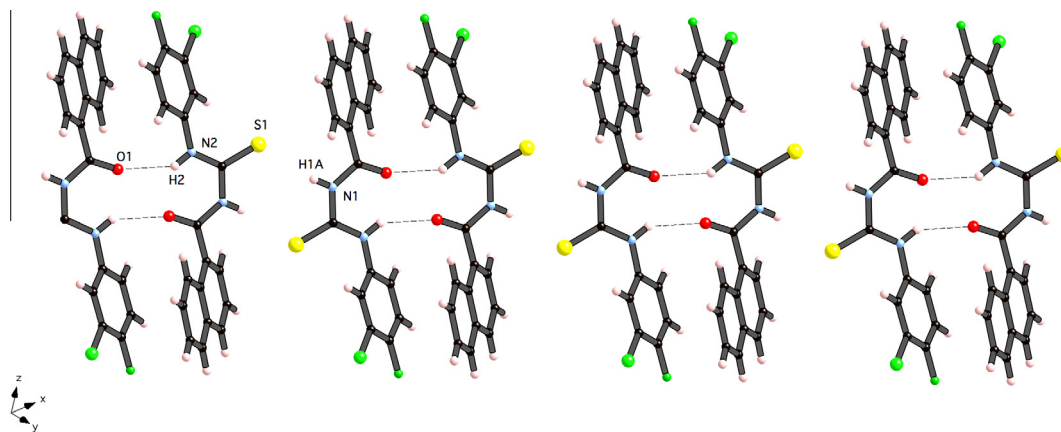


Fig. 4. Partial packing diagram for compound **2** showing the H-bonded and  $\pi$ -stacked chains extending down the  $xy$  direction in the crystal.

from boiling ethanol affords the products **1** and **2** as crystalline solids in good yields.

In  $^1\text{H}$  NMR spectra a singlet signals integrating 1H appeared in the  $\delta = 12\text{--}13$  ppm range, corresponding to the N1–H and N2–H protons of the thiourea group. The protons of the aromatic rings are observed in the typical region around  $\delta = 7.5$  ppm. The  $^{13}\text{C}$  NMR analysis further confirmed the structure of the title compound by displaying the characteristic signals for the thioamide (C=S) and the amide (C=O) carbons at  $\delta$  values of 182.5 and 179.6 ppm and at 171.4 and 170.4 ppm for compounds **1** and **2**, respectively. The FTIR spectral data shows the characteristic bands of the thiourea group at  $3169/3219\text{ cm}^{-1}$  ( $\nu\text{N-H}$ ),  $1679/1680\text{ cm}^{-1}$  ( $\nu\text{C=O}$ ), strong absorptions ca.  $1500\text{ cm}^{-1}$  for the  $\delta\text{N-H}$  and weak but defined peaks at  $739/847\text{ cm}^{-1}$  ( $\nu\text{C=S}$ ), for compounds **1/2**, respectively. Detailed analysis of the vibrational spectra is given in the following section.

#### Molecular and crystal structure

The X-ray structures of compounds **1** and **2** are shown in Figs. 1 and 2, respectively. Table 1 includes selected bond distances and angles derived from the structure refinements. The gas phase optimization for both structures is in good agreement with experimental data. Bond lengths and angles in the heavy atoms skeletons are very close with those previously reported [38,39].

As usual for 1-acyl-3-mono substituted thioureas, the molecular conformation of **1** and **2** is further stabilized by an intramolecular (N2–H2 $\cdots$ O1) hydrogen bond, which forms a pseudo-six-membered ring. Both compounds **1** and **2** are stabilized by intramolecular N–H $\cdots$ O=C hydrogen bond interactions of similar strength, characterized by the following parameters **1**: [N2 $\cdots$ O1 = 2.615(2) Å, N2–H2A $\cdots$ O1 = 140(2) $^\circ$ ] and **2**: [N2 $\cdots$ O1 = 2.6631(16) Å, N2–H2A $\cdots$ O1 = 135(2) $^\circ$ ]. These values are very well reproduced by the calculations, with N2 $\cdots$ O1 distances of 2.655 and 2.660 Å, and N2–H2A $\cdots$ O1 angles of 142 and 140 degrees for compounds **1** and **2**, respectively.

The 1-(acyl)-thiourea moiety for **1** compound is oriented almost planar forming an angle of S1/C12/N1/C11/O1 = 175.7(2) $^\circ$ , while for **2** compound the sulfur atom is twisted away from the carbonyl group giving rise to an angle S1/C12/N1/C11/O1 of 163.5(2) $^\circ$ .

From the conformational point of view, it is interesting to note that the C=O double bond in the amide group and the naphthyl rings are not co-planar, with nearly similar dihedral angles (48.4(1) $^\circ$  and 49.0(1) $^\circ$ ) for compounds **1** and **2**, respectively. More important differences are observed for the mutual orientation of the dihalo-substituted phenyl rings and the central 1-acyl thiourea plane. Thus, the pseudo-dihedral angle between the

2,4-di-fluoro phenyl ring and the C=S double bond is 69.4(1) $^\circ$ , whereas for the 3-chloro-4-fluoro phenyl ring is 46.7(1) $^\circ$ . It is plausible that the halogen substitution in the position 2 causes a high steric repulsion with the C=S group. Similar conformational features were reported for 1-(acyl)-3-(2-fluoro-phenyl) thioureas.[40]

The stabilization of the two compounds are also supported by weak N–H $\cdots$ O hydrogen bond interactions. Molecules of **1** and **2** both form hydrogen bonded dimers in the solid state held together by **1**: (N2 $\cdots$ O1 $^i$  = 3.180(2) Å N2–H2A $\cdots$ O1 $^i$  = 119(2) $^\circ$  ( $^i$  symm code 1–x, 1–y, –z) **2**: (N2 $\cdots$ O1 $^i$  = 3.000(2) Å N2–H2a–O3 $^i$  = 132(2) $^\circ$  ( $^i$  –x+2, –y+1, –z). Both structures are further stabilized by N–H $\cdots$ S hydrogen bonds **1**: (N1 $\cdots$ S1 $^{ii}$  = 3.395(1), N1–H2A $\cdots$ S1 $^{ii}$  = 171(2) $^\circ$  ( $^{ii}$  2–x, 1–y, –z) **2**: (N1 $\cdots$ S1 $^{ii}$  = 3.4860(15) Å, N1–H1A $\cdots$ S1 $^{ii}$  = 171(2) $^\circ$  ( $^{ii}$  1–x, –y, –z) resulting in infinite chains extending along the x direction in the case of **1** and along the xy direction in the case of **2** (Figs. 3 and 4). For compound **2**, the chains are further stabilized by  $\pi$ -stacking interactions between adjacent naphthalene and phenyl rings (tilt angle 11.43(4) $^\circ$ ), the distance between the centroid for the rings ranges from 3.485(2) to 3.915(2) Å.

#### Vibrational analysis

Tables 2 and 3 show the experimental and theoretical vibrational frequencies and their respective assignment for **1** and **2**. The analysis includes also a tentative vibrational assignment based on the comparison with reported data available in the literature for similar molecules [24,41–49]. As expected, most normal modes involve strong mixing of symmetry modes of the phenyl and naphthyl rings. The main features associated with the 1-acylthiourea core –C(O)NHC(S)NH– will be especially discussed. In particular, vibrational spectroscopy techniques have shown to be very informative regarding the presence of intramolecular hydrogen bond interactions involving the N–H donors. Medium intensity absorptions at  $3169$  and  $3157\text{ cm}^{-1}$  are found in the infrared spectra of compounds **1** and **2**, respectively, which can be associated with the  $\nu(\text{N2-H})$  stretching mode [50,51]. Results obtained by quantum chemical calculations show that the formation of the intramolecular N–H $\cdots$ O=C hydrogen bond produces a red-shift and a strong intensification of the  $\nu(\text{N2-H})$  normal mode as compared with the other thioamide  $\nu(\text{N1-H})$  stretching. Weak bands observed in the infrared spectra at  $3213$  and  $3219\text{ cm}^{-1}$  can be associated with the  $\nu(\text{N1-H})$  stretching modes of compounds **1** and **2**, respectively (see Tables 2 and 3). It should be noted also that the high intensity of the  $\nu(\text{N-H})$  displayed for 1-benzoyl substituted thioureas may be due to contribution of Fermi resonance effects with the  $\nu(\text{C=C})$  first overtone and/or  $\nu(\text{C=C}) + \delta(\text{N-H})$  combinations modes [52].



**Table 2**  
FTIR and FT-Raman experimental data for compound **1**, together with the values and tentative normal mode assignment.

Experimental <sup>a</sup>		Calculated <sup>b</sup>			Tentative assignment, PED (%) <sup>c</sup>
IR	Raman	Freq	IR int	Raman int	
3213 w, sh		3531	104	1.0	$\nu(\text{N1-H})$ (100)
3169 m		3210	351	5.1	$\nu(\text{N2-H})$ (100)
3145 m	3082 w	3153	120	1.9	$\nu(\text{C-H})$ phenyl (87)
3058 w	3068 m	3124	272	4.4	$\nu(\text{C-H})$ naphthyl (90)
3011 w	3053 w	3095	31	0.5	$\nu(\text{C-H})$ naphthyl (90)
1679 s	1680 m	1693	222	27.9	$\nu(\text{C=O})$ (75) + $\delta(\text{N2H})$ (12)
1663 m	1666 m	1614	56	8.1	$\nu(\text{C=C})$ phenyl (47) + $\delta(\text{N2H})$ (10)
1612 m	1618 m	1601	24	3.6	$\nu(\text{C=C})$ naphthyl (80)
1593 w		1587	238	35.9	$\nu(\text{C=C})$ naphthyl (65) + $\delta(\text{CCH})$ (11)
1535 vs	1538 w	1573	529	81.9	$\nu(\text{C=C})$ phenyl (20) + $\delta(\text{N2H})$ (35)
1520 sh, s	1512 w	1517	87	14.9	$\nu(\text{C=C})$ naphthyl (35) + $\delta(\text{N1H})$ (20)
1502 sh, s		1510	90	15.5	$\delta(\text{N2H})$ (40) + $\delta(\text{N1H})$ (10)
1462 w	1465 vw	1458	35	6.6	$\delta(\text{CH})$ naphthyl (40) + $\delta(\text{CCC})$ (15)
1437 m	1437 m	1438	19	3.8	$\nu(\text{C=C})$ naphthyl (40) + $\delta(\text{CH})$ naphthyl (15)
1371 w	1374 vs	1378	230	51.0	$\nu(\text{C=C})$ naphthyl (80)
1332 br, m		1350	97	22.9	$\nu_{\text{as}}(\text{NCN})$ (51) + $\nu(\text{C=C})$ naphthyl (37)
1302 s	1302 m	1293	97	25.6	$\nu(\text{C=C})$ phenyl (64) + $\nu_{\text{as}}(\text{NCN})$ (15)
1281 m	1284 w	1264	33	9.3	$\delta(\text{CH})$ naphthyl (81)
1262 m		1251	10	3.0	$\delta(\text{CH})$ phenyl (75)
1191 m	1186 vw	1180	21	6.9	$\delta(\text{CH})$ naphthyl (43) + $\delta(\text{CH})$ phenyl (25)
1152 vs	1160 br, w	1143	75	27.3	$\nu_{\text{s}}(\text{NCN})$ (65) + $\nu(\text{CN1C})$ (20)
1141 vs	1146 vw	1139	43	15.7	$\delta(\text{NCN})$ (48) + $\delta(\text{CH})$ phenyl (10)
1130 sh, m		1134	8	3.1	$\nu(\text{C-F})$ (35) + $\delta(\text{CH})$ phenyl (52)
1097 m	1096 vw	1116	12	0.1	$\nu_{\text{s}}(\text{CNC})$ (64) + $\delta(\text{CH})$ phenyl (15)
	1065 m	1075	35	14.8	$\delta(\text{CH})$ naphthyl (34) + $\delta(\text{CH})$ phenyl (25)
1023 vw	1025 vw	1029	17	8.3	$\delta(\text{CH})$ naphthyl (63)
968 m		960	3	2.0	$\delta(\text{CH})$ phenyl (55) + $\delta(\text{CCC})$ phenyl (20) + $\nu(\text{C-F})$ (15)
865 m	867 w	865	25	18.4	$\delta(\text{CCC})$ phenyl (35) + $\delta(\text{CCC})$ naphthyl (25)
849 m	851 w	838	1	0.5	oop (N2H) (28) + oop (CH) phenyl (42)
804 m		801	1	0.7	oop (CH) naphthyl (70)
793 sh, m		786	1	0.6	$\delta(\text{CCC})$ naphthyl (75)
779 s		780	19	17.4	$\delta(\text{CCC})$ naphthyl (45) + oop (CH) naphthyl (36)
756 m	755 w	773	48	45.2	oop (CH) naphthyl (68)
739 m	732 w	745	33	34.2	$\nu(\text{C=S})$ (44) + $\rho(\text{N2H})$ (15)
730 w, sh		735	5	4.0	oop (N2H) (51) + $\nu(\text{C=S})$ (11)
721 vw		725	2	2.0	oop (C) phenyl (78)
695 br, w		707	1	3.0	oop (C) phenyl (70) + $\delta(\text{CH})$ phenyl (15)
659 w	662 ww	659	16	17.0	$\delta(\text{CCC})$ phenyl (45) + oop N1H (23)
654 w		652	26	10.0	oop (N1H) (54) + oop CH naphthyl (18)
638 vw		642	22	3.0	oop (N1H) (46) + oop CH naphthyl (22)
624 vw	620 vw				oop (N1H) (55)
614 vw		606	1	1.0	oop (FCCC) (55) + oop CS (15)
569 m	570 vw	563	17	18.0	$\delta(\text{CCC})$ phenyl (45) + oop (C) naphthyl (22)
521 vw	524 vw	530	6	12.0	$\delta(\text{CCC})$ (naphthyl + phenyl) (68)
506 vw	508 m	514	5	23.0	$\delta(\text{CCC})$ (naphthyl + phenyl) (72)
462 br, m		454	3	8.1	oop (C) naphthyl (54)
415 m		405	1	2.4	$\delta(\text{CCC})$ phenyl (37) + oop (C) naphthyl (24) +
	379 vw	383	3	13.0	oop (C) phenyl (60) + $\delta(\text{CCC})$ naphthyl (11)
	367 w	361	7	34.1	$\delta(\text{CCC})$ phenyl (32) + $\delta(\text{CNC})$ (21)
	249 w	246	3	30.6	oop (C) naphthyl (66)

<sup>a</sup> Band intensities and shape: vs = very strong; s = strong; m = medium; w = weak; vw = very weak, sh: shoulder, br: broad.<sup>b</sup> Scaled computed values for the S form, IR intensities in km/mol.<sup>c</sup>  $\nu$ : Stretching (subscripts s and as refer to symmetric and antisymmetric modes, respectively),  $\delta$ : deformation, oop: out of plane deformation modes.

The analysis of the infrared and Raman spectra in the  $\nu(\text{C=O})$  stretching mode region is also of main interest for analyzing the presence of the intramolecular hydrogen bond [53]. For compound **1**, this mode is observed at  $1679\text{ cm}^{-1}$  in the infrared spectrum and  $1680\text{ cm}^{-1}$  in Raman (calculated  $1693\text{ cm}^{-1}$ ) and strong infrared absorption at  $1680\text{ cm}^{-1}$ , with counterparts at  $1682\text{ cm}^{-1}$  in the Raman spectra for compound **2** (calculated  $1685\text{ cm}^{-1}$ ). These values are in good agreement with those previously reported for related 1-(1-naphthyl)-3,3-disubstituted thioureas [20].

In analogy with the vibrational properties for thioamide bond, the  $\delta(\text{N-H})$  deformation mode in 1-acylthioureas is usually referred as thioamide band I, in general appearing as very intense absorption in the  $1500\text{--}1600\text{ cm}^{-1}$  region [53]. In the present case this spectral range is quite overcrowding due to contributions from the  $\nu(\text{C=C})$  normal modes of the phenyl and naphthyl moieties.

The infrared spectra show very strong and rather broad absorptions at around  $1535$  ( $1538\text{ cm}^{-1}$  Raman) and  $1534\text{ cm}^{-1}$  ( $1531\text{ cm}^{-1}$  Raman) for **1** and **2**, respectively, which can be assigned to  $\delta(\text{N2-H})$ , in agreement with previous works [23]. The other  $\delta(\text{N1-H})$  deformation mode appears at lower wavenumbers, also as medium-intensity absorptions at  $1502$  and  $1505\text{ cm}^{-1}$  ( $1493\text{ cm}^{-1}$ , Raman), respectively [3,54].

The thioamide band II, mainly associated with the  $\nu_{\text{as}}(\text{NCN})$  stretching, is observed as broad bands at  $1332\text{ cm}^{-1}$  in the infrared spectra for both compounds. This normal mode of vibration is sensitive to the substitution 3,3-disubstituted thioureas and appears at higher wavenumbers (up to  $1395\text{ cm}^{-1}$ ) than that of the 3-monosubstituted ones (below  $1350\text{ cm}^{-1}$ ), as previously reported [3]. The calculated values for **1** and **2** are  $1350$  and  $1361\text{ cm}^{-1}$ , respectively, very close to the experimental ones.

**Table 3**  
FTIR and FT-Raman experimental data for compound **2**, together with the calculated values and tentative normal mode assignment.

Experimental <sup>a</sup>		Calculated <sup>b</sup>		Tentative assignment, PED (%) <sup>c</sup>	
IR	Raman	Freq	IR int Raman int		
3219 br, m		3531	40	1.0	$\nu(\text{N1-H})$ (100)
3157 br, m		3226	485	5.6	$\nu(\text{N2-H})$ (100)
	3086 m	3124		4.2	$\nu(\text{C-H})$ naphthyl (96)
3057 w	3068 m	3121	17	4.1	$\nu(\text{C-H})$ naphthyl (93)
	3046 m	3107		0.6	$\nu(\text{C-H})$ naphthyl (90)
1680 s	1682 m	1685	118	29.0	$\nu(\text{C=O})$ (73) + $\delta(\text{N2H})$ (12)
	1579 m	1586		38.5	$\nu(\text{C=C})$ naphthyl (66)
1534 vs, br	1531 m	1571	535	69.2	$\delta(\text{HN2})$ (42) + $\nu(\text{C=C})$ phenyl (33)
1505 sh, s	1511 sh, w	1517		14.5	$\nu(\text{C=C})$ naphthyl (60) + $\delta(\text{N1H})$ (21)
	1493 m	1507	364	11.7	$\delta(\text{HN1})$ (35) + $\nu(\text{C-N2})$ (22) + $\delta(\text{CCH})$ naphthyl (14)
	1462 vw	1457		7.0	$\delta(\text{CCH})$ naphthyl (54) + $\delta(\text{CCC})$ naphthyl (16)
	1437 w	1435		12.6	$\delta(\text{CH})$ naphthyl (58) + $\nu(\text{C=C})$ naphthyl (22)
1404 vw	1404 vw	1402	16	2.8	$\nu(\text{C=C})$ phenyl (68) + $\delta(\text{CH})$ phenyl (15)
	1373 vs	1391	25	27.7	$\delta(\text{CH})$ naphthyl (67)
1332 br, w	1333 br, vw	1361	258	36.6	$\nu_{\text{as}}(\text{NCN})$ (57) + $\delta(\text{N1H})$ (15)
1295 vw	1295 vw	1349	87	19.2	$\nu_{\text{as}}(\text{NCN})$ (55)
1282 vw	1282 vw, sh	1324	260	10.8	$\nu(\text{C=C})$ naphthyl (77)
1268 s	1270 m	1269	205	5.2	$\delta(\text{CH})$ naphthyl (33) + $\delta(\text{CCC})$ naphthyl (25) + $\nu(\text{C=C})$ naphthyl (17)
1259 m		1262	113	14.1	$\nu(\text{C-F})$ (25) + $\delta(\text{CH})$ naphthyl (20) + $\nu(\text{C=C})$ naphthyl (14)
1249 m	1249 w	1252	16	4.1	$\delta(\text{CH})$ phenyl (68)
1215 m	1215 w	1235	21	44.5	$\delta(\text{CH})$ naphthyl (55) + $\nu(\text{C1-C11})$ (13)
1191 m	1192 vw	1205	19	18.5	$\delta(\text{CH})$ phenyl (51) + $\nu(\text{C13-N2})$ (10)
1169 sh, m	1169 w	1181	20	23.5	$\delta(\text{CH})$ naphthyl (62)
1160 s	1158 w	1146	189	56.5	$\nu_{\text{s}}(\text{NCN})$ (38) + $\delta(\text{CH})$ (22) + phenyl (21)
1125 m	1125 br, w	1128	38	6.4	$\delta(\text{CH})$ phenyl (81)
1071 w	1071 vw	1076	9	11.0	$\nu(\text{C=C})$ naphthyl (63) + $\delta(\text{CH})$ naphthyl (21)
1060 m	1060 w	1047	25	3.3	$\delta(\text{CCC})$ naphthyl (55) + $\nu(\text{C-Cl})$ (26) + $\delta(\text{CH})$ phenyl (15)
1025 w	1026 vw	1029	15	8.0	$\delta(\text{CH})$ naphthyl (68)
1009 w		993	2	4.7	$\delta(\text{CCC})$ naphthyl (72)
	965 br, vw	974		1.0	oop (CH) naphthyl (75)
916 vvw	916 vw	918	1	0.4	oop (CH) naphthyl (69)
890 w	888 br, w	884	25	2.4	$\delta(\text{CCC})$ (62) + $\delta$ OCN (25)
874 m	874 vw	876	19	0.2	oop(C-H) naphthyl (70) + $\delta(\text{CCC})$ phenyl (15)
847 vvw	846 s	843	1	66.3	$\nu(\text{C=S})$ (22) + $\delta(\text{CCC})$ naphthyl (15) + $\delta(\text{CCC})$ phenyl (14)
825 w	825 w	826	78	1.4	oop (N2H) (65) + oop (CH) phenyl (25)
807 w		801	29	0.8	oop (C-H) naphthyl (59) + oop (C-H) phenyl (26)
787 br, m	780 vvw	776	7	7.4	oop (N2H) (45) + oop (CH) phenyl (23)
714 vvw		724	5	2.3	oop (CH) naphthyl (58) + $\delta(\text{CNC})$ (31)
704 m	704 m	675	46	40.4	$\nu(\text{C-Cl})$ (26) + $\nu(\text{C=S})$ (15) + $\delta(\text{CCC})$ naphthyl (27)
678 w	680 m	659	19	21.0	$\delta(\text{CCC})$ phenyl (46) + $\delta(\text{CCC})$ naphthyl
662 w	662 m	650	27	3.4	oop (N1-H) (57)
619 w	617 br, w	639	17	3.4	oop (N1-H) (25) + $\delta(\text{CNC})$ (23)
575 w	577 vw	580	5	0.2	oop (C) phenyl (62)
562 vw	562 vw	565	20	26.9	oop (C) naphthyl (64)
523 vw	507 m	517	3	33.2	$\delta(\text{CCC})$ naphthyl (58)
	467 vw	468		2.7	oop(C12) (52) + $\delta(\text{CCC})$ naphthyl (18)
	448 w	460		22.3	oop (C) phenyl (85) + oop (C) phenyl (12)
	431 w	442		0.7	oop (C) naphthyl (72)
	374 m	388		25.1	$\delta(\text{CIC})$ (45) + $\delta(\text{SCN2})$ (25)
	356 w	355		12.1	$\delta(\text{SCN1})$ (58) + $\delta(\text{SCN2})$ (28)

<sup>a</sup> Band intensities and shape: vs = very strong; s = strong; m = medium; w = weak; vw = very weak, sh: shoulder, br: broad.

<sup>b</sup> Scaled computed values for the S form, IR intensities in km/mol.

<sup>c</sup>  $\nu$ : stretching (subscripts s and as refer to symmetric and antisymmetric modes, respectively),  $\delta$ : deformation, oop: out of plane deformation modes.

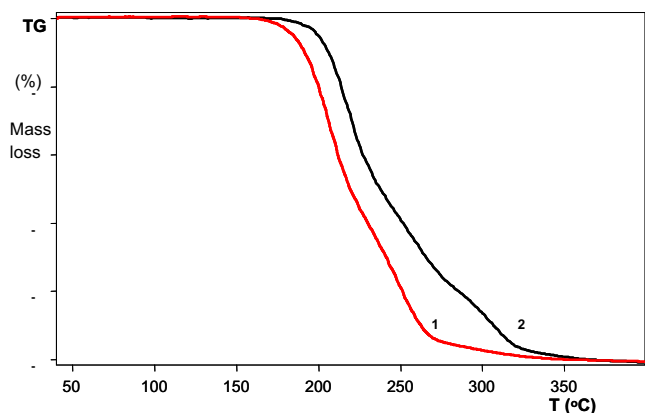
The  $\nu_{\text{s}}(\text{NCN})$  stretching mode is usually assigned to the thioamide band III. For the thiourea molecule [55], the symmetric motion of the C–N stretching occurs at around 1150  $\text{cm}^{-1}$  [56,57]. In the present case, following the quantum chemical calculation description, the  $\nu_{\text{s}}(\text{NCN})$  modes of **1** and **2** are assigned to the 1152 (1160) and 1160 (1158)  $\text{cm}^{-1}$  intense absorptions found in the infrared (Raman values in parentheses) spectra, respectively, also in agreement with previous work on similar species [58].

Finally, the  $\nu(\text{C=S})$  stretching mode (thioamide band IV) of 1-acylthiourea compounds is found around in the 600–800  $\text{cm}^{-1}$  range [3,4,59,60], but higher wavenumbers values (up to 1100  $\text{cm}^{-1}$ ), are also reported [44,48]. These differences suggest that the  $\nu(\text{C=S})$  stretching mode is very sensitive to the presence of an intermolecular interactions involving the C=S group [41], which originates an intense Raman dispersion due to the polarizability of the C=S bond [61]. With the aid of DFT calculations, we

assigned this mode to the absorptions observed at 739 and 847  $\text{cm}^{-1}$ , with counterparts in the Raman spectra at 732 and 846  $\text{cm}^{-1}$ , for compounds **1** and **2**, respectively.

#### Thermal behavior

Fig. 5 shows the thermogravimetric curves for the two synthesized compounds in order to compare their thermal behavior. The analysis of the DTG curves reveals the compound **1** decomposes in two step over the temperature range of 180–380 °C. The first decomposition stage occurs in the temperature range of 180–230 °C with a mass loss of 54.3% consistent with the evolution of the 1-(acyl)-thiourea moiety and the dihalo-substituted phenyl rings (loss of weight calculated 54.6%). The second step is compatible with a mass loss of 45.7% and might be attributed to the evolution of the naphthalene group (calculated 45.2%).



**Fig. 5.** TGs curves for compounds **1** (red) and **2** (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 5, the TGs curves indicate a similar thermal behavior for both compounds here studied. Compound **2** decomposes at slightly higher temperature than the other one. This higher thermal stability of compound **2** probably arise because in its crystal packing the chains are further stabilized by  $\pi$ -stacking between adjacent naphthalene and phenyl rings, as discussed previously. In general, the thermal behavior displayed by compounds **1** and **2** are in agreement with the previously reported for related compounds [62,63].

#### UV-Vis spectra

Fig. 6 shows the experimental and calculated electronic spectra of both compounds in DMSO in the 200–800 nm range. The UV/Vis spectra are evaluated from the calculated vertical electronic transitions energies and oscillator strengths between the initial and final states. A good correlation between the experimental and computed spectra of **1** and **2** is achieved. The assigned transitions with major contributions for **1** and **2** are shown in Table 4.

For a better description of the electronic properties, the character of the orbitals involved in the main electronic transitions, together with their energy (in eV), for compounds **1** and **2** are shown in Fig. 7.

In the experimental spectrum two principal bands centered at 296 nm for both compounds are observed, having a rather broad feature. Four calculated transitions with relevant oscillator strengths are correlated with the appointed bands. For compound **1**, this band correlated with HOMO–2  $\rightarrow$  LUMO,

**Table 4**

Calculated absorption wavelength (nm) and oscillator strengths of the most significant excited states for **1** and **2**.

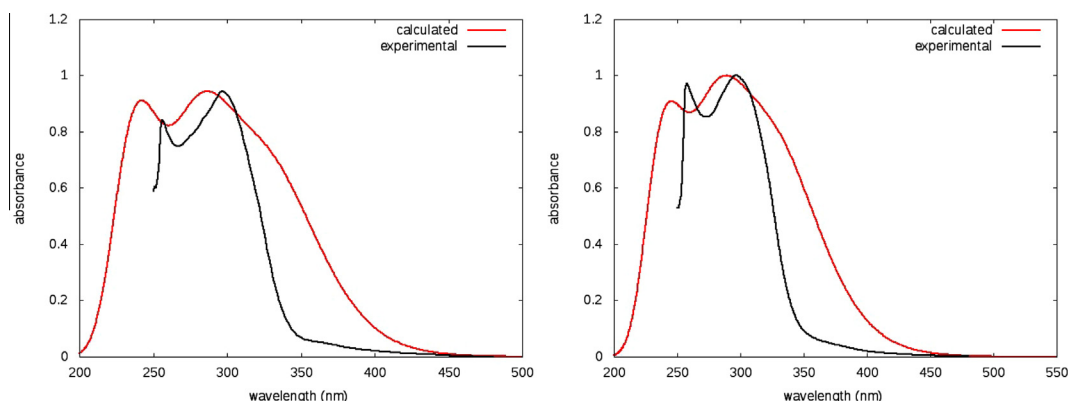
Wavelength (nm)	Oscillator strength		Assignment	
	Experimental	Calculated		
<b>Compound 1</b>				
296		327.6	0.2063	HOMO–2 $\rightarrow$ LUMO (95%)
		287.1	0.2331	HOMO–3 $\rightarrow$ LUMO (36%)
256		240.8	0.1349	HOMO $\rightarrow$ LUMO+1 (57%)
		235.7	0.1506	HOMO–3 $\rightarrow$ LUMO+1 (84%)
258		238.4	0.1357	HOMO $\rightarrow$ LUMO+4 (79%)
		238.4	0.1357	HOMO $\rightarrow$ LUMO+4 (74%)
<b>Compound 2</b>				
296		328.2	0.2191	HOMO–2 $\rightarrow$ LUMO (95%)
		290.8	0.1657	HOMO–3 $\rightarrow$ LUMO (47%)
258		287.1	0.2331	HOMO–4 $\rightarrow$ LUMO (34%)
		238.4	0.1357	HOMO–3 $\rightarrow$ LUMO (57%)
258		238.4	0.1357	HOMO $\rightarrow$ LUMO+4 (74%)
		238.4	0.1357	HOMO $\rightarrow$ LUMO+4 (74%)

HOMO–3  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO+1 transitions, while for **2** also the HOMO–4  $\rightarrow$  LUMO and HOMO–3  $\rightarrow$  LUMO transitions contribute. Experimental peak at 256 and 258 nm in the experimental UV spectra for **1** and **2**, respectively, are correlated with HOMO–3  $\rightarrow$  LUMO+1 and HOMO  $\rightarrow$  LUMO+4 transitions for **1**, and HOMO  $\rightarrow$  LUMO+4 transition for **2**.

The HOMO corresponds to a  $\pi$  bonding system localized over phenyl moiety and a p-type orbital strongly located on the atom of sulfur. The HOMO–2 corresponds to a  $\pi$  bonding system localized over naphthalene moiety and a p-type orbital strongly located on the atom of sulfur similar as the described one for HOMO. Both HOMO–3 and HOMO–4 contain  $\pi$  bonding electronic density located in the phenyl moiety and a p system over thiourea region. The LUMO has  $\pi$  symmetry with antibonding nature delocalized over the naphthyl and the thiourea groups. In LUMO+1 the electron density of  $\pi^*$  nature is extended all over the molecule. The LUMO+4 is constituted by a p system delocalized over all molecule. The delocalization of electrons within the thiourea moiety is also dependent in some extend on the substituents. Thus, the HOMO–LUMO transition has a  $\pi \rightarrow \pi^*$  character and involves the electron transfer from the phenyl ring to the 1-naphthyl thiourea group.

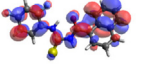
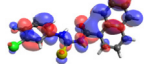
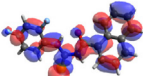
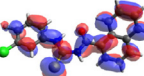
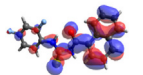
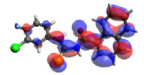
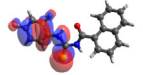
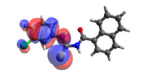
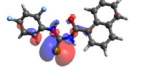
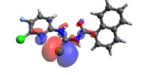
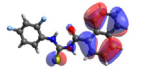
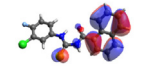
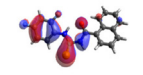
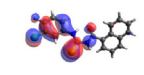
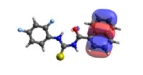
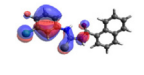
#### Conclusion

The conformational and structural properties have been determined for two novel 1-(1-naphthyl)-3-(halo-phenyl) substituted thioureas. The X-ray molecular structures for both compounds here studied show that the central  $-\text{C}(\text{O})\text{NHC}(\text{S})\text{NH}-$  moiety



**Fig. 6.** Experimental and simulated UV-Vis spectra of compounds **1** (left) and **2** (right) in DMSO.



Type	Compound 1	Compound 2
LUMO+4		
	-0.66 eV	-0.77 eV
LUMO+1		
	-1.70 eV	-1.75 eV
LUMO		
	-2.46 eV	-2.54 eV
HOMO		
	-6.43 eV	-6.45 eV
HOMO-1		
	-6.47 eV	-6.51 eV
HOMO-2		
	-6.76 eV	-6.83 eV
HOMO-3		
	-7.34 eV	-7.32 eV
HOMO-4		
	-7.50 eV	-7.47 eV

**Fig. 7.** Plots of the frontier molecular orbitals calculated for **1** and **2** molecules in gas phase. Computed energies are also given.

adopts the typical six membered ring structure favored by strong C=O...H-N intramolecular hydrogen bond. Intermolecular N-H...O and N-H...S hydrogen bond interactions dominate the crystal packing of **1** and **2**. Furthermore, a  $\pi$ -stacking interaction between adjacent naphthalene and phenyl rings is observed for compound **2**. Both compounds are thermally stable up to ca. 180 °C, compound **2** is slightly more stable than compound **1**. The vibrational and electronic properties were fully determined

by the combined analysis of experimental spectroscopic data with quantum chemical calculations. The effect of 3-substitution on the 1-(1-naphthyl)thiourea group was determined, including the first assignment of the electronic spectra in terms of detailed quantum chemical calculations.

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