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

Aamer Saeed a,⇑, Saba Ashraf a, Jonathan M. White b, Delia B. Soria c, Carlos A. Franca c, Mauricio F. Erben c,⇑

a Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan
b Bio-21 Institute, School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia
c CEQUINOR (UNLP, CONICET-CCT La Plata), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, 1900 La Plata, Argentina

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 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.

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...
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 \(-\text{C}(\text{O})\text{NH}2\text{S}\) moiety is preferred for 1-(acyl/aryloyl)-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–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 Br2 in chloroform (Hugershoff reaction) was determined. The capabilities of (1-naphthyl)-arylamidine compounds as ligand were investigated and their Cu2+, Ni2+ and Pd2+ 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 i-laroyl)-3-(mono-substituted) thioureas [23,24], here we report the preparation and spectroscopic characterization of two closely related thioureas having the 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 13C NMR spectra were determined in DMSO-d solution 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).

Infrared spectra were recorded in KBr pellets with a resolution of 2 cm\(^{-1}\) in the 4000–400 cm\(^{-1}\) range on a Bruker EQUINOX 55 FTIR spectrometer (Argentina). The FT-Raman spectra were recorded 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\(^{-1}\). 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 nm resolution).

Thermal analyses were performed with Shimadzu TGA-50 unit, between room temperature and 500 °C, at a heating rate of 5 °C/min and nitrogen flow of 50 ml/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\(_l\)) using the following relationship [32]:

\[
I_l = I_i (v_o - v_i) A_S/v_i[1 - exp(-hv_i/kT)]
\]

where \(v_o\) is the exciting wavenumber (in cm\(^{-1}\) units); \(v_i\) is the vibrational wave number of the ith 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 an 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 \(\lambda = 0.71073\) Å). The temperature during both data collections was maintained at 130(0)K.

**Crystal data for 1: C\(_{18}\)H\(_{12}\)F\(_2\)OS, M = 342.36, T = 130.0(2) K, \(\lambda = 0.7107\) Å, Monoclinic, space group P21/c \(a = 10.8284(3), b = 6.8539(16), c = 21.2605(5)\) Å, \(\beta = 104.55(2)°\), \(V = 1527.26\) (6) Å\(^3\), \(Z = 4, D_0 = 1.489\) Mg M\(^{-3}\), \(\mu (\text{Mo-K}\alpha) = 0.241\) mm\(^{-1}\), F(000) = 704, crystal size 0.67 \(\times\) 0.49 \(\times\) 0.24 mm. \(I_{\text{max}} = 32.28°\), 17,375 reflections measured, 4,995 independent reflections \((R_{\text{int}} = 0.0292)\) the final R = 0.0384 \((I > 2\sigma(I)), 4,149\) data and wR(F\(^2\)) = 0.0995 (all data) GOOF = 1.045, CCDC 896972.

**Crystal data for 2: C\(_{18}\)H\(_{12}\)ClF\(_2\)OS, M = 358.81, T = 130.0(2) K, \(\lambda = 0.7107\) Å, Triclinic, space group P-1 \(a = 7.3692(3), b = 7.4218(3), c = 15.4693(7)\) Å, \(\alpha = 81.896(4)°\), \(\beta = 76.505(4)°\), \(\gamma = 88.369(3)°\), \(V = 814.45(6)\) Å\(^3\), \(Z = 2, D_0 = 1.463\) Mg M\(^{-3}\), \(\mu (\text{Mo-K}\alpha) = 0.380\) mm\(^{-1}\), F(000) = 368, crystal size 0.50 \(\times\) 0.36 \(\times\) 0.05 mm. \(I_{\text{max}} = 32.17°\), 9709 reflections measured, 5165

![Scheme 1](image-url) Representation of the S conformer in 1-(1-naphthoyl)-3-(mono) substituted thioureas.
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

| Compound                | Parameter | Bond distances (Å) | | Bond angles (°) |
|-------------------------|-----------|--------------------|-----------|
| Bond distances          |           |                    |           |
| C12=Si                  | 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                  |
| Sodium angles           |           |                    |           |
| S1                      | 123.9(2)  | 129.5              | 125.4(1)  | 129.7                  |
| O1                      | 122.7(1)  | 122.4              | 122.7(1)  | 122.4                  |
| O2                      | 122.7(1)  | 122.4              | 122.7(1)  | 122.4                  |
| O3                      | 122.7(1)  | 122.4              | 122.7(1)  | 122.4                  |
| Dihedral angles         |           |                    |           |
| S1=Si=12=N1C11          | 176.1(2)  | 178.7              | 168.6(2)  | 178.6                  |
| O1=C11=C12C10           | 48.4(6)   | 40.5              | 49.0(5)  | 40.5                  |

**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 50 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.

**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 of the final thioureas as crude solids. Re-crystallization from ethanol to afford thioureas 1 and 2.

![Fig. 3. Partial packing diagram for compound 1 showing the H-bonded chains extending along the x direction in the crystal.](Image)
from boiling ethanol affords the products 1 and 2 as crystalline solids in good yields.

In $^1$H NMR spectra a singlet signals integrating 1H appeared in the $\delta = 12–13$ 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 $^{13}$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 FTR spectral data shows the characteristic bands of the thiourea group at 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 for the thioamide group. The protons of the aromatic rings are very well reproduced by the calculations, with N2–H and weak but defined peaks at 739/847 cm$^{-1}$ (νC=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⋅⋅⋅O1) hydrogen bond, which forms a pseudo-six-membered ring. Both compounds 1 and 2 are stabilized by intramolecular N–H ⋅⋅⋅O=C hydrogen bond interactions of similar strength, characterized by the following parameters: 1: [N2⋅⋅⋅O1 = 2.615(2) Å, N2–H2A⋅⋅⋅O1 = 140(2)°] and 2: [N2⋅⋅⋅O1 = 2.663(16) Å, N2–H2A⋅⋅⋅O1 = 135(2)°]. These values are well reproduced by the calculations, with N2⋅⋅⋅O1 distances of 2.655 and 2.660 Å, and N2–H2A⋅⋅⋅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)°, 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)°.

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)° and 49.0(1)°) 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)°, whereas for the 3-chloro-4-fluoro phenyl ring is 46.7(1)°. 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 ⋅⋅⋅O hydrogen bond interactions. Molecules of 1 and 2 both form hydrogen bonded dimers in the solid state held together by 1: (N2⋅⋅⋅O1 = 3.180(2) Å N2–H2A⋅⋅⋅O1 = 119(2)° (I symm code 1–x, 1–y, 1–z) 2: (N2⋅⋅⋅O1 = 3.000(2) Å N2–H2A⋅⋅⋅O3 = 132(2)° (I–x+2,–y+1,–z). Both structures are further stabilized by N–H ⋅⋅⋅S hydrogen bonds 1: (N1⋅⋅⋅S1 = 3.395(1) Å, N1–H2A⋅⋅⋅S1 = 171(2)° (ii 2–x,1–y,–z) 2: (N1⋅⋅S1 = 3.4860(15)Å, N1–H1A⋅⋅⋅S1 = 171(2)° (ii 1–x,–y,–z) resulting in infinite chains extending along the x direction of 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 π-stacking interactions between adjacent naphthalene and phenyl rings (tilt angle 11.43(4)°), 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)NH(C(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 cm$^{-1}$ are found in the infrared spectra of compounds 1 and 2, respectively, which can be associated with the ν(N2–H) stretching mode [50,51]. Results obtained by quantum chemical calculations show that the formation of the intramolecular N–H⋅⋅⋅C hydrogen bond produces a red-shift and a strong intensification of the ν(N2–H) normal mode as compared with the other thioamide ν(N1–H) stretching. Weak bands observed in the infrared spectra at 3213 and 3219 cm$^{-1}$ can be associated with the ν(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 ν(N–H) displayed for 1-benzoxy substituted thioureas may be due to contribution of Fermi resonance effects with the ν(C=C) first overtones and/or ν(C=C) + ν(N–H) combinations modes [52].

![Fig. 4. Partial packing diagram for compound 2 showing the H-bonded and π-stacked chains extending down the xy direction in the crystal.](image-url)
The infrared and Raman experimental data for compound 1, together with the values and tentative normal mode assignment.

| Experimental | Calculated | Tentative assignment, PED (%) |
|--------------|------------|--------------------------------|
| **IR**       | **Raman**  | **Freq** | **IR int** | **Raman int** |  |
| 3213 w, sh   | 3531       | 104      | 1.0        | ν(N−H) (100)  |
| 3169 m       | 3210       | 351      | 5.1        | ν(N2−H) (100) |
| 3145 m       | 3082       | w        | 120        | ν(C−H) phenyl (87) |
| 3058 w       | 3068 m     | 3124     | 272        | 4.4          |
| 3011 w       | 3053 m     | 3095     | 31         | 0.5          |
| 1679 s       | 1680 m     | 1693     | 222        | 27.9         |
| 1663 m       | 1666 m     | 1614     | 56         | 8.1          |
| 1612 m       | 1618 m     | 1601     | 24         | 3.6          |
| 1593 w       | 1587       | 238      | 35.9       |
| 1535 vs      | 1538 w     | 1573     | 529        | 81.9         |
| 1520 sh, s   | 1512 w     | 1517     | 87         | 14.9         |
| 1502 sh, s   | 1510       | 90       | 15.5       |
| 1462 w       | 1465 vw    | 1458     | 35         | 6.6          |
| 1437 m       | 1437 m     | 1438     | 19         | 3.8          |
| 1371 w       | 1374 vs    | 1378     | 230        | 51.0         |
| 1332 br, m   | 1350       | 97       | 22.9       |
| 1302 s       | 1302 m     | 1293     | 97         | 25.6         |
| 1281 m       | 1284 w     | 1264     | 33         | 9.3          |
| 1262 m       | 1251       | 10       | 3.0        |
| 1191 m       | 1188 vw    | 1180     | 21         | 6.9          |
| 1152 vs      | 1160 br, w | 1143     | 75 vs      | 27.3         |
| 1141 vs      | 1146 vw    | 1139     | 43         | 15.7         |
| 1130 sh, m   | 1134       | 8        | 3.1        |
| 1097 m       | 1096 vvw   | 1116     | 12         | 0.1          |
| 1065 m       | 1075       | 35       | 14.8       |
| 1023 vvw     | 1025 vvw   | 1029     | 17         | 8.3          |
| 968 m        | 960        | 3        | 2.0        |
| 865 m        | 867 w      | 865      | 25         | 18.4         |
| 849 m        | 851 w      | 838      | 1         | 0.5          |
| 804 m        | 801        | 1        | 0.7        |
| 7931 sh, m   | 7866       | 780      | 19         | 17.4         |
| 779 s        | 780        | 19        | 17.4       |
| 756 m        | 755 w      | 773      | 48         | 45.2         |
| 739 m        | 732 w      | 745      | 33         | 34.2         |
| 730 w, sh    | 735        | 5        | 4.0        |
| 7152 vs      | 725 w      | 725      | 10         | 2.0          |
| 695 br, w    | 707        | 1        | 3.0        |
| 659 w        | 662 vvw    | 659      | 16         | 17.0         |
| 654 w        | 652        | 26       | 10.0       |
| 638 vvw      | 642        | 22       | 3.0        |
| 624 vvw      | 620 vvw    | 600      | 1         |
| 614 vvw      | 614 vvw    | 570 vvw  | 563        | 17          |
| 569 m        | 570 vvw    | 563      | 17         | 18.0         |
| 521 vvw      | 524 vvw    | 530      | 6          | 12.0         |
| 506 vvw      | 508 m      | 514      | 5          | 23.0         |
| 462 br, m    | 454        | 3        | 8.1        |
| 415 m        | 405        | 1        | 2.4        |
| 379 vw       | 383        | 3        | 13.0       |
| 367 w        | 361        | 7        | 34.1       |
| 249 w        | 246        | 3        | 30.6       |

\[a\] Band intensities and shape: vs = very strong; s = strong; m = medium; w = weak; vw = very weak, sh: shoulder, br: broad.

\[b\] Scaled computed values for the S form, IR intensities in km/mol.

\[c\] ν: Stretching (subscripts s and as refer to symmetric and antisymmetric modes, respectively), δ: deformation, oop: out of plane deformation modes.

The infrared and Raman spectra in the ν(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 1769 cm⁻¹ in the infrared spectrum and 1680 cm⁻¹ in Raman (calculated 1693 cm⁻¹) and strong infrared absorption at 1680 cm⁻¹, with counterparts at 1682 cm⁻¹ in the Raman spectra for compound 2 (calculated 1685 cm⁻¹). These values are in good agreement with those previously reported for related 1-(1-naphthoyl)-3,3-disubstituted thioureas [20].

In analogy with the vibrational properties for thioamide bond, the δ(N−H) deformation mode in 1-acythioureas is usually referred as thioamide band I, in general appearing as very intense absorption in the 1500–1600 cm⁻¹ region [53]. In the present case this spectral range is quite overcrowding due to contributions from the ν(C=O) normal modes of the phenyl and naphthyl moieties. The infrared spectra show very strong and rather broad absorptions at around 1535 (1538 cm⁻¹ Raman) and 1534 cm⁻¹ (1531 cm⁻¹) for 1 and 2, respectively, which can be assigned to δ(N2−H), in agreement with previous works [23]. The other δ(N1−H) deformation mode appears at lower wavenumbers, also as medium-intensity absorptions at 1502 and 1505 cm⁻¹ (1493 cm⁻¹, Raman), respectively [3,54].

The thioamide band II, mainly associated with the νas(NCN) stretching, is observed as broad bands at 1332 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 cm⁻¹) than that of the 3-monosubstituted ones (below 1350 cm⁻¹), as previously reported [3]. The calculated values for 1 and 2 are 1350 and 1361 cm⁻¹, respectively, very close to the experimental ones.
The $\nu_{(NCN)}$ 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 cm$^{-1}$ [56,57]. In the present case, following the quantum chemical calculation description, the $\nu_{(NCN)}$ modes of 1 and 2 are assigned to the 1152 (1160) and 1160 (1158) 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 $\nu(C=S)$ stretching mode (thioamide band IV) of 1-acythiourea compounds is found around in the 800–600 cm$^{-1}$ range [34,59,60], but higher wavenumbers values (up to 1100 cm$^{-1}$), are also reported [44,48]. These differences suggest that the $\nu(C=S)$ 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 cm$^{-1}$, with counterparts in the Raman spectra at 732 and 846 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%).
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 π-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 → LUMO,

\[
\text{HOMO} \rightarrow \text{LUMO} \quad \text{and} \quad \text{HOMO} \rightarrow \text{LUMO+1} \quad \text{transitions, while for} \quad 2 \quad \text{also the} \quad \text{HOMO} \rightarrow \text{LUMO} \quad \text{and} \quad \text{HOMO} \rightarrow \text{LUMO} \quad \text{transitions contribute. Experimental peak at 256 and} \quad 258 \quad \text{nm in the experimental UV spectra for} \quad 1 \quad \text{and} \quad 2, \quad \text{respectively, are correlated with} \quad \text{HOMO} \rightarrow \text{LUMO+1} \quad \text{and} \quad \text{HOMO} \rightarrow \text{LUMO+4} \quad \text{transitions for} \quad 1, \quad \text{and} \quad \text{HOMO} \rightarrow \text{LUMO+4} \quad \text{transition for} \quad 2.
\]

The HOMO corresponds to a π bonding system localized over phenyl moiety and a p-type orbital strongly located on the atom of sulfur. The HOMO–2 corresponds to a π 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 π bonding electronic density located in the phenyl moiety and a p system over thiourea region. The LUMO has π symmetry with antibonding nature delocalized over the naphthyl and the thiourea groups. In LUMO+1 the electron density of π* 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 π → π* character and involves the electron transfer from the phenyl ring to the 1-napthyl 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 —C(O)NH— moiety

---

**Table 4**

| Wavelength (nm) | Oscillator strength | Assignment                  |
|----------------|---------------------|-----------------------------|
| Compound 1     |                     |                             |
| 296            | 327.6 0.2063        | HOMO–2 → LUMO (95%)         |
|                | 287.1 0.2331        | HOMO–3 → LUMO (36%)         |
|                | 256               240.8 0.1349 | HOMO–3 → LUMO+1 (84%)       |
|                | 235.7 0.1506        | HOMO → LUMO+4 (79%)         |
| Compound 2     |                     |                             |
| 296            | 328.2 0.2191        | HOMO–2 → LUMO (95%)         |
|                | 290.8 0.1657        | HOMO–3 → LUMO (47%)         |
|                | 287.1 0.2331        | HOMO–4 → LUMO (34%)         |
|                | 258               238.4 0.1357 | HOMO → LUMO+4 (74%)         |

---

**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.)

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

**Acknowledgments**

MFE and DBS are members of the Carrera del Investigador of CONICET (República Argentina). The Argentinean author thanks to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the ANPCYT and to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata for financial support.

**References**

[1] A.R.L. Fraga, C.L. Destri, G. Forte, A. Rescifina, F. Punzo, Could N-(diethylcarbamothioyl)benzamide be a good ionophore for sensor membranes?, J. Mol. Struct. 981 (2010) 86–92.

[2] D. Wilson, M.Á. Arada, S. Alegría, M. del Valle, Lead(II) ion selective electrodes with PVC membranes based on bis-thioureas as ionophores: 1,3-bis(N-benzoylthiourea)benzene and 1,3-bis(N-furoylthiourea)benzene, J. Hazard. Mater. 181 (2010) 140–146.

[3] O. Estévez-Hernández, E. Otazo-Sánchez, J.L. Hidalgo-Hidalgo de Cisneros, I. Naranjo-Rodríguez, E. Reguera, A Raman and infrared study of 1-furyl-3-mono-substituted and 3,3-disubstituted thioureas, Spectrochim. Acta A 62 (2005) 964–971.

[4] E. Otazo-Sánchez, P. Ortiz-del-Toro, O. Estévez-Hernández, L. Pérez-Marin, I. Goicoechea, A. Cerón Beltran, J.R. Villagómez-Ibarra, Aroylthioureas: new organic ionophores for heavy metal ion selective electrodes. A nuclear magnetic resonance study, Spectrochim. Acta A 58 (2002) 2281–2290.

[5] M. Boiocchi, L. Del Beca, D.E. Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, Nature of urea-fluoro interaction: incipient and definitive proton transfer, J. Am. Chem. Soc. 126 (2004) 16507–16514.

[6] M. Bonizzoni, L. Fabbrizzi, A. Taglietti, F. Tiengo, (Benzylideneamino)thioureas – chromogenic Interactions with Anions and N-H Deprotonation, Eur. J. Org. Chem. 2006 (2006) 3567–3574.

[7] H.-L. Chen, Z.-F. Guo, Z.-L. Lu, Controlling ion-sensing specificity of n-amiidothioureas: from anion-selective sensors to highly Zn²⁺-selective sensors by tuning electronic effects, Org. Lett. 14 (2012) 5070–5073.

[8] S. Li, X. Cao, C. Chen, S. Kė, Novel salicylic acid-oriented thiourea-type receptors as colorimetric chemosensor: synthesis, characterizations and selective naked-eye recognition properties, Spectrochim. Acta A 96 (2012) 18–23.

[9] J. Sun, S. Cai, H. Mei, J. Li, N. Yan, Q. Wang, Z. Lin, D. Huo, Molecular docking and qsar studies on substituted acyl(thio)urea and thiaiodazol [2,3-¿] pyrimidine derivatives as potent inhibitors of influenza virus neuraminidase, Chem. Biol. Drug Des. 76 (2010) 245–254.

[10] C. Limhan, A-V. Missir, L.C. Chinta, A.F. Neagu, C. Draghici, M.C. Chifiriu, Synthesis and antimicrobial evaluation of some new 2-(4-fluoro-phenoxy)benzoic acid thioureides, Rev. Chim. (Bucharest) 62 (2011) 168–173.

[11] A. Saeed, U. Flörke, M.F. Erben, A review on the chemistry, coordination, structure and biological properties of 1-(acylaryl)–3-[(substituted) thioureas, J. Sulfur Chem. 35 (2014) 318–355.

[12] A. Okuniewski, J. Chojnacki, B. Becker, 3,3-Dibenzoyl-1,1-dibenzylo-1,1-ethane-1,2-diyli(thio)urea, Acta Crystallogr. E 68 (2012) o619–o620.

[13] A. Saeed, A. Khurshid, J.P. Jasinski, C.G. Pozzi, A.C. Fantoni, M.F. Erben, Competing intramolecular NH·OC hydrogen bonds and extended intermolecular network in 1-(4-chlorobenzoyl)-3-(2-methyl-4-oxopentan-2-yl) thiourea analyzed by experimental and theoretical methods, Chem. Phys. 431–432 (2014) 39–46.

[14] J. Duque, O. Estévez-Hernández, E. Reguera, R.S. Correa, P. Cutierrez, Maria, 1-(2-Furoyl)-3-(1-naphthyl)thiourea, Acta Crystallogr. E 64 (2008) o1068.

[15] S. Saeed, N. Rashid, J.P. Jasinski, J.A. Golen, 1-Benzoyl-3-(naphthalen-1-yl)thiourea, Acta Crystallogr. E 67 (2011) o3187.

[16] D.P. Singh, S. Prapat, S.K. Gupta, R.J. Butcher, 1-(Naphthalen-1-yl)-3-[(thiophen-2-yl)carbonyl]thiourea, Acta Crystallogr. E 68 (2012) o2882–o2883.

[17] C.K. Özer, H. Arslan, D. VanDerveer, N. Külcü, Synthesis and characterization of N-(arylcarbamothioyl)-cyclohexanecarboxamide derivatives: the crystal structure of N-(Naphthalen-1-yl)carbamothioyl)cyclohexanecarboxamide, Molecules 14 (2009) 655–666.

[18] H. Arslan, U. Flörke, N. Külcü, Synthesis, characterization, and crystal structure of 1-(4-chloro-benzoyl)-3-naphthalen-1-yl-thiourea, J. Chem. Crystallogr. 33 (2003) 919–924.

[19] H. Arslan, D.S. Mansuroglu, D. VanDerveer, G. Binzet, The molecular structure and vibrational spectra of N-(2,2-di phenylacetyl)-N-(naphthalen-1-yl)-thiourea by Hartree–Fock and density functional methods, Spectrochim. Acta A 72 (2009) 561–571.
[20] M. Dzurilla, P. Kutschy, J. Imrich, S. Brtoš, Hugershoff reaction of N-1- or N-2-naphthyl-N'-monosubstituted and N', N'-disubstituted thiourea derivatives, Collect. Czech. Chem. Commun. 59 (1994) 2663–2676.

[21] U. Schröder, R. Richter, L. Beyer, J. Angulo-Cornejo, M. Lino-Pachoeco, A. Guileen, Metallkomplexe naphthyl-substituierter thioamidosterverbindungen, Z. Anorg. Allg. Chem. 629 (2003) 1051–1058.

[22] H.-T. Du, H.-J. Du, W. Zhou, 3,3'-Di-(2-fluorophenyl)-1,1'- (o-phenylene)thiourea, Acta Crystallogr. E 64 (2008) o1780.

[23] A. Saeed, M.F. Erben, U. Schröder, R. Richter, L. Beyer, J. Angulo-Cornejo, M. Lino-Pachoeco, A. Guileen, Metallkomplexe naphthyl-substituierter thioamidosterverbindungen, Z. Anorg. Allg. Chem. 629 (2003) 1051–1058.

[24] J. Dillen, M.G. Woldu, K.R. Koch, N,N-(Heptane-2,6-diyl)-N,N-dimethylthiocarbamate, Spectrochim. Acta A 49 (1993) 2623–2633.

[25] H. Arslan, U. Flörke, N. Külci, Theoretical studies of molecular structure and vibrational spectra of O-ethyl benzoylthioicarbamate, Spectrochim. Acta A 67 (2007) 936–943.

[26] S. Torrico-Vallejo, M.F. Erben, R. Boese, O.E. Piro, E.E. Castellano, C.O. DellaVedova, Védová, Structural effects and hydrogen bonds on N,Nênciaeacutemed(CH₃CO)₂S⁺⁺⁺⁺⁺, studied by experimental and theoretical methods, J. Mol. Struct. 918 (2009) 146–153.

[27] A. Saeed, M.F. Erben, N. Abbas, U. Flörke, Synthesis, crystal X-ray diffraction structure, vibrational properties and quantum chemical calculations on 1-(4-fluorobenzamido)phenyl)-1-(4-fluorobenzamido)thiourea, J. Mol. Struct. 984 (2010) 240–245.

[28] Z. Rekikov, L. Baouzong, Z. Liming, D. Jiangang, Z. Yong, L. Lude, Y. Xujie, Structural and spectral studies on N-(4-chloro)benzoyl-N'(4-tolyl)thiourea, J. Mol. Struct. 690 (2004) 145–150.

[29] H. Arslan, N. Külci, U. Flörke, Normal coordinate analysis and crystal structure of N,N-dimethyl-N'(2-chloro)benzoylthiourea, Spectrochim. Acta A 64 (2006) 1065–1071.

[30] A. Saeed, M.F. Erben, M. Bolte, Synthesis, structural and vibrational properties of 1-(adamantan-1-carboxylic acid)-3-halophenylthioicarbamates, Spectrochim. Acta A 102 (2013) 408–413.

[31] M. Atis, F. Karipcin, B. Sarıboğa, M. Taş, H. Çelik, Structural, antimicrobial and computational characterization of 1-benzoyl-3-(5-chloro-2-fluorophenyl)thiourea, Spectrochim. Acta A 98 (2012) 290–301.

[32] O. Hrizová, J. Černák, P. Safar, Z. Frohlichová, I. Coregh, Furans substituted phenylthioureas: spectral studies, semi-empirical quantum-chemical calculations and X-ray structure analyses, J. Mol. Struct. 743 (2005) 29–48.

[33] M.S.M. Yusof, R.H. Jusoh, W.M. Kairali, B.M. Yamin, Synthesis and characterisation of a series of N-(3,4-dichlorophenyl)-N,N,N-dimethyl-N'-methoxybenzoylthioureas, J. Mol. Struct. 975 (2010) 280–284.

[34] A. Saeed, M.F. Erben, U. Flörke, Effect of fluorine substitution on the crystal structures and vibrational properties of phenylthiourea isomers, J. Mol. Struct. 982 (2010) 91–99.

[35] K. Srinivasan, S. Gunasekaran, S. Krishnan, Spectroscopic investigations and structural confirmation studies on thiourea, Spectrochim. Acta A 70 (2010) 1171–1175.

[36] W. Kolodziejczyk, I. Wawer, K. Wozniak, J. Klimowski, Hydrogen bonding and the structure of substituted ureas: solid-state NMR, vibrational spectroscopy, and single-crystal X-ray diffraction studies, J. Phys. Chem. A 97 (1993) 12147–12152.

[37] D.P. Singh, S. Pratap, S.K. Gupta, R.J. Butcher, Structural and spectral speciation on methyl 2-(3-furan-2-carbonyl)thioureaed benzolate: a comparative experimental and theoretical study, J. Mol. Struct. 1048 (2013) 500–509.

[38] Y. Mido, I. Kitagawa, M. Hashimoto, H. Matsuura, Vibrational spectra and normal coordinate analysis of N-methylthiourea and three deuterated analogues, Spectrochim. Acta A 55 (1999) 2623–2633.

[39] W. Yang, W. Zhou, Z. Zhang, Structural and spectroscopic study on N-2-fluorobenzoyl-N,N′-4-methoxyphenylthiourea, J. Mol. Struct. 828 (2007) 46–53.

[40] L. Otazo-Sanchez, L. Perez-Marin, O. Estevez-Hernandez, S. Rojas-Lima, J. Alonso-Chamarro, Aroythiourates: new organic ionophores for heavy-metal ion selective electrodes, J. Chem. Soc., Perkin Trans. 2 (2001) 2211–2218.

[41] Z. Popovic, D. Matkovic-Calogovic, Z. Soldin, G. Pavlovic, N. Davidovic, D. Vikic-Topic, Mercury(II) compounds with 1,3-iodimidazol-2-thione and its 1-methyl analogue. Preparative and NMR spectroscopic studies. The crystal structures of di-miodo-bis[iodo-(1,3-iodimidazol-2-thiolato-5)mercury(ll)] and bis[iodo-(1,3-iodimidazol-2-thiolato-5)mercury(ll)], Inorg. Chim. Acta 294 (1999) 35–46.

[42] Z. Dan, H. Jee, S. Jiri-rong, Z. Yi-tang, W. Li-qin, H. Jian-yun, Synthesis, crystal structure and thermal analysis of N,N,N′-2-(dimethylamino)phenyl)-N,N,N′-4-fluorobenzoylthiourea, Spectrochim. Acta A 55 (1999) 2623–2633.

[43] A.J. Daud, W.M. Kairali, H. Mohamed-Zuki, K. KuBulat, Synthesis and characterization of N-4-Aminophenylethenylbenzonitrile)-N'-1-naphthylthiourea as single molecular chemosensor for carbon monoxide sensing, J. Sulfur Chem. 35 (2014) 691–699.