Journal of Molecular Structure 1065-1066 (2014) 150–159

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

The role of substituents in the molecular and crystal structure of 1-(adamantane-1-carbonyl)-3-(mono)- and 3,3-(di) substituted thioureas

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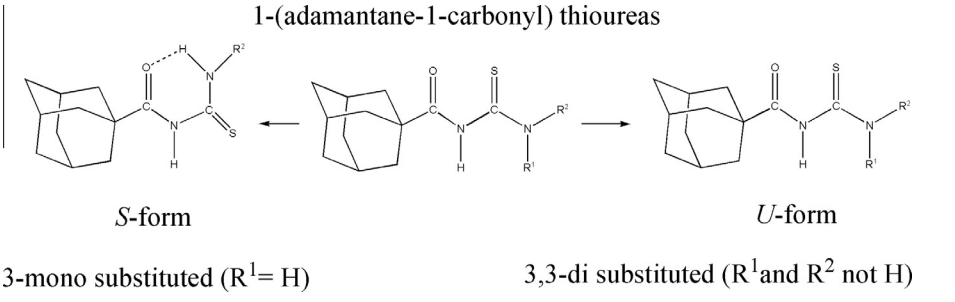
HIGHLIGHTS

- Three 1-(adamantane-1-carbonyl)-3-substituted thioureas were prepared for the first time.
- Crystal and molecular structures were determined.
- Both intra- and inter-molecular hydrogen bonds are found in the crystal.
- Conformational aspects are discussed in terms of the vibrational spectra.
- The role of the substituent attached to the thiourea group is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 December 2013
Received in revised form 11 February 2014
Accepted 3 March 2014
Available online 11 March 2014

Keywords:
Acyl thioureas
Vibrational spectroscopy
Quantum chemical calculations
Crystal structure
Hydrogen bond
Conformational analysis

ABSTRACT

Three novel 1-(adamantane-1-carbonyl) thioureas were synthesized by the reaction of adamantyl isothiocyante with corresponding amines and fully characterized by spectroscopy methods. Two isomeric species, i.e. 1-(adamantane-1-carbonyl)-3-(3-nitrophenyl)thiourea (**1**) and 1-(adamantane-1-carbonyl)-3-(4-nitrophenyl)thiourea (**2**), are structurally characterized and a third related compound, namely 1-(adamantane-1-carbonyl)-3,3-(methyl-phenyl)thiourea (**3**) has been also included for assessing the role of the nitrogen substitution on the structural properties. As determined by X-ray analysis, compounds **1** and **2** exhibit the *S* conformation with the C=O and C=S double bonds in a pseudo-antiperiplanar orientation, whereas the *U* form is found for compound **3**. These conformational features are mainly dictated by the substitution degree on the thiourea core and the ability of forming an intra-molecular N—H···O=C hydrogen bond for mono-substituted analogues **1** and **2**. These dissimilar interactions affect the vibrational properties, which have been determined by infrared and Raman spectroscopies and quantum chemical calculations at the B3LYP/6-311++G** level of approximation.

1. Introduction

As early as 1873, Neucki reported the preparation of $CH_3C(O)NHC(S)NH_2$, which is considered the first synthesized 1-acyl thiourea derivative. Substitution can occur on the second nitrogen atom affording compounds with general formula $RC(O)NHC(S)NR^1R^2$. These are useful materials for the synthesis of a wide variety of heterocyclic compounds [1,2], as ionophores in ion selective electrodes [3–5] and versatile "collectors" used in mineral extraction by froth flotation processes [6,7]. Moreover, the potential application of this kind of compounds as smoothened antagonist has been highlighted recently [8], and its antiviral

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http://dx.doi.org/10.1016/j.molstruc.2014.03.002
0022-2860/

properties has been proved [9]. Review articles covering the synthesis [10], the coordination chemistry [11,12], potential applications [10] and biological aspects of 1-acyl thioureas can be found in the chemical literature [13].

There are, however, only a few examples in the literature of ureas/thioureas containing the adamantyl group [14]. Accordingly, thioureas containing the bulkier 1-adamantyl group have been used as organocatalysts for synthesis of enantiomerically pure α- and β-amino acids [15] and *N*-(1-adamantyl)-*N*′-(4-guanidino-benzyl)urea is a highly selective non-peptidic uPA inhibitor and a lead structure for the development of potent antimetastatic drugs [16]. Similarly *N*-adamantyl-*N*′-phenylurea derivatives are simple soluble epoxide hydrolase (sEH) inhibitors [17]. A library of 1600 adamantyl ureas was screened in vitro for anti tuberculosis activity and for increasing the bioavailability of inhibitors of human soluble epoxide hydrolase (hsEH) [18].

The use of the adamantyl group has a multidimensional significance in drug design. The hydrophobic substituent constant and steric factors increase the drug stability and plasma half-life of this kind of compounds [19], as recently demonstrated for polyhydroxylated *N*-benzylbenzamide derivatives containing an adamantyl moiety [20]. Adamantyl-1,3,4-oxadiazoles and adamantylamino-1,3,4-thiadiazoles show antimicrobial, and anti-inflammatory activities [21]; adamantyl triazoles are selective inhibitors of 11β-hydroxysteroid dehydrogenase type 1 [22] as are the thiazolidine derivatives with an adamantyl group [23]. 1-Adamantane carboxylic acid hydrazides have promising antimicrobial activity [24]. In this context, it should be noted that the medicinal chemistry of adamantane derivatives has been recently reviewed [25].

In continuation of our work focused on the chemistry and structure of acyl-thiourea compounds, herein we report the synthesis and structural characterization of three novel 1-(adamantane-1-carbonyl)-3-substituted thioureas (R = 1-CO—$C_{10}H_{15}$). Specifically, two isomeric mono-substituted derivatives with R^1 = H and R^2 = 3-NO_2—C_6H_4 and 4-NO_2—C_6H_4 (**1** and **2**, respectively) and the di-substituted species 1-(adamantane-1-carbonyl)-3,3-(methylphenyl)thiourea (R^1 = —CH_3, R^2 = C_6H_5) (**3**) are studied. The selected species allowed scrutinizing the role of nitrogen substitution on the conformational properties of the 1-(adamantane-1-carbonyl)thiourea moiety. For this purpose, the molecular and crystal structure for the three species have been determined by X-ray diffraction and the vibrational properties analyzed by a combined experimental (including infrared and Raman spectroscopy) and theoretical calculations at the B3LYP/6-311++G** level of approximation.

2. Experimental

2.1. General

Adamantane carboxylic acid, 3-nitroaniline and 4-nitroaniline and *N*-methylaniline were the commercial products from Aldrich. Analytical grade acetone (E. Merck) was dried and freshly distilled prior to use. Melting points were recorded using a digital Gallenkamp (SANYO) model MPD.BM 3.5 apparatus and are uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ at 300 MHz and 75.4 MHz respectively using a Bruker spectrophotometer. Fourier transform infrared spectroscopy (FTIR) spectra for pure solids were recorded using Bio-Rad Excalibur FTS 3000 MX spectrophotometer (Madison, Wisconsin, USA) in the ATR mode of analysis. Mass Spectra (EI, 70 eV) on a gas chromatography–mass spectrometry (GC–MS) instrument Agilent technologies, and elemental analyses were conducted using a LECO-183 CHNS analyzer.

Furthermore, solid-phase (as KBr pellets) infrared spectra were recorded with a resolution of 2 cm^{-1} in the 4000–400 cm^{-1} range on a Bruker EQUINOX 55 FTIR spectrometer. The FT-Raman spectra of powdered samples 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}.

Computational details. Quantum chemical calculations were performed with the GAUSSIAN 03 program package [26]. The molecular geometries were optimized to standard convergence criteria by using B3LYP DFT hybrid methods employing the Pople-type [27] extended valence triple-ξ basis set augmented with diffuse and polarization functions in both the hydrogen and weighty atoms [6-311++G**]. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found. Scott and Radom derived the scaling factors for the theoretical harmonic vibrational frequencies at 19 levels utilizing a total of 1066 individual vibrations for small molecules [28]. Zhou and coworkers [29] demonstrated that scaled B3LYP calculations are powerful approaches for understanding the vibrational spectra of medium-sized organic compounds and the recommended factors of 0.96 was used to scale the theoretical frequencies.

2.2. X-ray data collection and structure refinement

Data were collected at 130(2) K on a Bruker AXS SMART APEX CCD diffractometer using Mo Kα radiation. Structures solved by direct methods [30], full-matrix least-squares refinement on F^2. 467/8167 Parameters/unique intensities for **1**, 233/4181 for **2** and 424/8250 for **3**, respectively. All but H atoms refined anisotropically, H atoms from difference Fourier maps refined on idealized positions with U_{iso} = 1.2 U_{eq}(C/N) or 1.5U_{eq}(C methyl) and C—H distances of 0.95–0.98 Å, H(N)-positions were refined freely. H(C_{methyl}) for **3** were allowed to rotate but not to tip. For **1** and **3** there are each two crystallographically independent molecules A and B per asymmetric unit with numbering schemes 1xx for A and 2xx for B, respectively. Experimental data are listed in Table 1, and Figs. 1–3 show the molecular structures.

2.3. Synthesis and general procedure

Adamantane-1-carbonyl isothiocyanate was prepared by reaction of adamantane-1-carbonyl chloride (10 mmol) and ammonium thiocyanate (10 mmol) in acetone (30 ml) under nitrogen. A solution of the suitable substituted aniline (10 mmol) in acetone (10 ml) was added and the reaction mixture refluxed for 2–4 h. The reaction mixture was then poured into cold water and the precipitated thioureas were recrystallized by slow evaporation from the ethyl acetate–chloroform (2:1) mixture.

*1-(Adamantane-1-carbonyl)-3-(3-nitrophenyl)thiourea (**1**):* yield 70%, mp 161–162 °C. FT-IR (ATR (solid), ν cm^{-1}): 3321, 2853, 2849, 1681, 1544, 1516, 1350, 1153, 889, 869. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.08 (br s, 1H, NH, D_2O exchangeable); 9.58 (br s, 1H, NH, D_2O exchangeable); 8.61 (s, 1H, Ar); 7.89 (d, 2H, *J* = 2.6 Hz Ar), 7.97 (d, 2H, *J* = 2.6 Hz Ar), 2.1 (brs, 3H, adamantane—CH), 1.96 (s, 6H, adamantane—CH_2), 1.83 (m, 6H, adamantane—CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): 179.4 (C=S); 178.7 (C=O), 145.0 (Ar), 144.3 (Ar), 124.5 (Ar), 122.9 (Ar), 120.6 (Ar), 41.9, 39.4, 38.5, 36.4, 36.0, 31.6, 28.0, 27.7, (adamantane—Cs). EI-MS, *m*/*z* (Rel. Int.): 221 (14), 202 (17), 180, 179, 163 (100), 135 (88), 137 (28), 122, 93, 80, 79, 67, 41, 39. Anal. Calcd for $C_{18}H_{21}N_3O_3S$ (359.44): C, 60.15; H, 5.89; N, 11.69; S, 8.92%; Found: C, 59.95; H, 5.83; N, 11.72; S, 8.97%.

*1-(Adamantane-1-carbonyl)-3-(4-nitrophenyl)thiourea (**2**):* yield 70%, mp 165 °C, FT-IR (ATR (solid), ν cm^{-1}): 3310, 2849, 1686, 1547, 1508, 1350, 1299, 1150, 896, 852. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.08 (br s, 1H, NH, D_2O exchangeable); 8.58 (br s, 1H, NH, D_2O

Table 1
Crystal data and structure refinement for compounds **1**–**3**.[a]

Compound	**1**	**2**	**3**
Empirical formula	C_{18} H_{21} N_3 O_3 S	C_{18} H_{21} N_3 O_3 S	C_{19} H_{24} N_2 O S
Formula weight	359.4	359.4	328.5
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P* $2_1/n$	*P* $2_1/c$	*P* $2_1/n$
a (Å)	7.2067(7)	12.6285(10)	21.627(5)
b (Å)	17.2759(16)	9.8576(8)	7.7396(18)
c (Å)	27.553(3)	14.1746(11)	21.627(5)
β (°)	94.185(2)	107.507(2)	107.09
V (Å^3)	3421.2(6)	1682.8(2)	3460.2(14)
Z	8	4	8
Dc (Mg m^{-3})	1.396	1.419	1.261
Absorp. coeff. (mm^{-1})	0.212	0.216	0.194
F(000)	1520	760	1408
Crystal size (mm^3)	0.43 × 0.28 × 0.12	0.42 × 0.29 × 0.25	0.49 × 0.37 × 0.30
h	$9 \leqslant h \leqslant 9$	−16/16	−28/28
k	$-22 \leqslant k \leqslant 21$	−13/13	−10/10
l	$-36 \leqslant l \leqslant 36$	−17/18	−28/28
Data collected	31,617	16,009	31,923
Unique reflections	8167	4181	8250
R(int)	0.041	0.029	0.036
Parameters	467	233	424
GooF	1.02	1.03	1.03
R^1 [*I* > 2sigma(*I*)]	0.044	0.043	0.055
wR^2 (all data)	0.111	0.121	0.149
Max/min Δ*F* (e Å−3)	0.38/−0.22 e Å^{-3}	0.58/−0.26	0.94/−0.86
CCDC deposition	882901	882900	912608

[a] Further conditions and refinement comments: temperature 130(2) K, wavelength 0.71073 Å. Absorption correction: semi-empirical from equivalents. Refinement method: full-matrix least-squares on F^2.

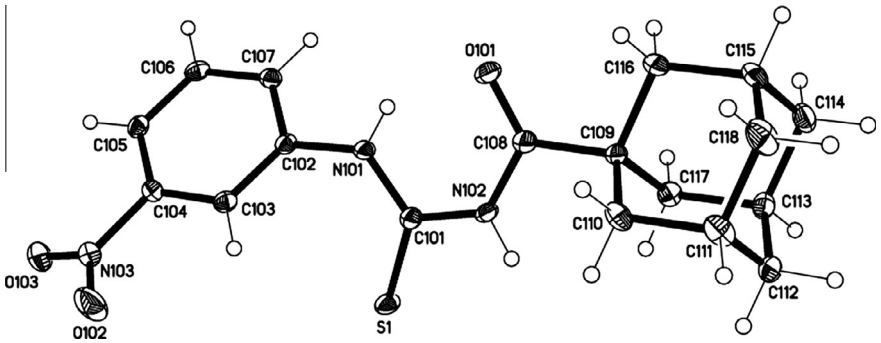


Fig. 1. Molecular structure of **1** with displacement ellipsoids plotted at 50% probability level. Only one molecule A shown.

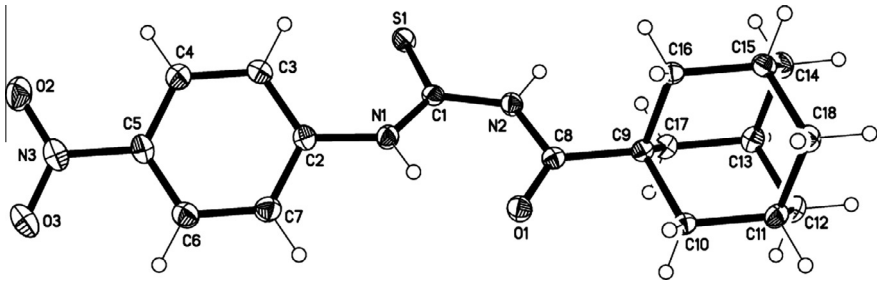


Fig. 2. Molecular structure of **2** with displacement ellipsoids plotted at 50% probability level.

exchangeable); 8.26 (d, 2H, *J* = 8.6 Hz, Ar), 8.0 (d, 2H, *J* = 8.6 Hz, Ar), 2.12 (brs, 3H, adamantane—CH), 1.93 (s, 6H, adamantane—CH_2), 1.80 (m, 6H, adamantane—CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$): 179.1 (C═S); 178.5 (C═O), 145.0 (Ar), 144.7 (Ar), 124.5 (Ar); 122.9 (Ar), 42.0, 41.9, 39.2, 38.5, 36.4, 36.0, 31.6, 28.0, 27.7, (adamantane—Cs). EIMS, *m*/*z* (Rel. Int.): 221 (11), 180, 179, 163 (100), 135 (69), 137 (33), 122, 93, 80, 79, 67, 41, 39. Anal. Calcd for C_{18}-$H_{21}N_3O_3S$ (359.44): C, 60.15; H, 5.89; N, 11.69; O, 13.35; S, 8.92%; Found: C, 59.03; H, 5.86; N, 11.73; S, 8.87%.

1-(Adamantane-1-carbonyl)-3,3-(methyl-phenyl)thiourea (***3***)*:* yield 74%, mp 115 °C. FT-IR (ATR (solid), ν cm^{-1}): 2906, 1700, 1508, 1435, 1376, 1224, 1184, 1118, 871, 800. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.83 (br s, 1H, NH, D_2O exchangeable); 7.23–7.33 (m, 3H, Ar); 7.38–7.43 (m, 2H, Ar); 3.17 (s, 3H, N—CH_3); 2.08 (s, 3H, adamantane—CH), 1.69 (s, 6H, adamantane—CH_2), 1.58 (q, 6H, adamantane—CH_2, *J* = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 182.2 (C═S); 169.92 (C═O); 143.05 (C-9); 45.47 (N—CH_3), 41.51, 39.25, 38.69, 38.49, 36.44, 28.05, 27.78, (adamantane—C).

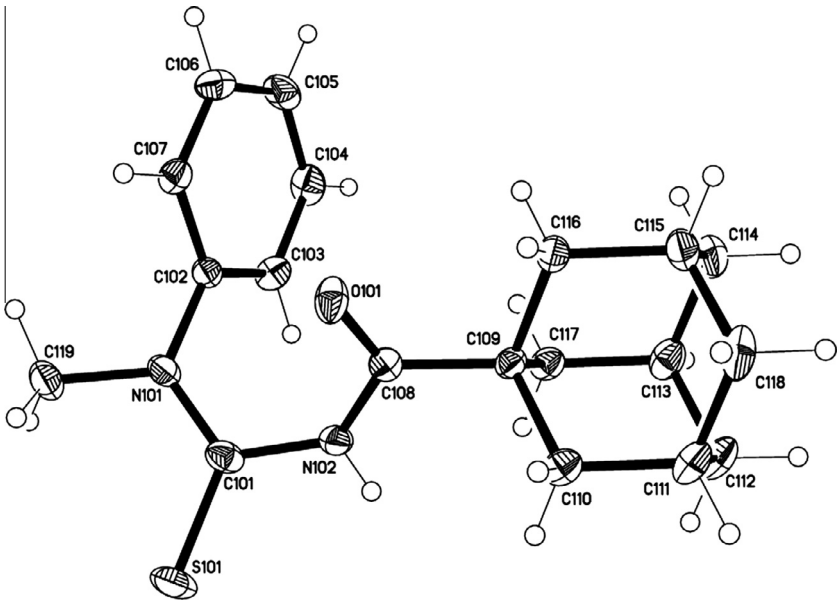


Fig. 3. Molecular structure of **3** with displacement ellipsoids plotted at 50% probability level. Only one molecule A shown.

EIMS, *m*/*z* (Rel. Int.): 328 (M^+, 41), 313, 222, 179 (42), 163 (100), 135 (88), 149 (23), 122, 106, 93, 80. Anal. Calcd for $C_{19}H_{24}N_2OS$ (328.47): C, 69.47; H, 7.36; N, 8.53; S, 9.76%; Found: C, 69.51; H, 7.40; N, 8.56; S, 9.71%.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of title acyl thioureas was adapted from the original method of Douglas–Dains [31] involving the reaction of acyl isothiocyanates produced *in situ* with suitable anilines in dry acetone or acetonitrile [32]. A similar method was recently used for the synthesis of related adamantyl thioureas [33]. Thus, freshly prepared adamantane-1-carbonyl isothiocyanate was treated with an equimolar quantity of 3-nitro-, 4-nitro- and *N*-methylaniline respectively in acetone to afford compounds **1**–**3**, respectively (Scheme 1).

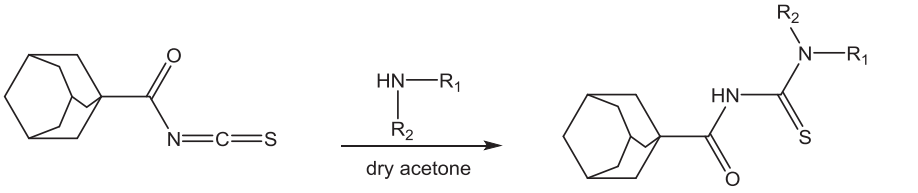
In the ^{1}H NMR the characteristic signals of adamantyl moiety: a 6H quartet at δ 1.75–1.79 (adamantane—CH_2), a 6H, singlet at 1.95–1.98 (adamantane—CH_2) and a 3H, singlet around 2.08 (adamantane—CH), besides singlets at δ 8.5–8.7 and 12.7–13.0 ppm were observed for HN(1) and HN(2) except for the secondary amine (**3**) where the HN(2) was absent. In the ^{13}C NMR characteristic signals at for adamantyl moiety at δ 27.7, 36.1–36.4, 38.6–38.5 and 41.5 ppm, as well those at δ = 182–179 ppm for thiocarbonyl and δ = 170–178 ppm for carbonyl carbons were observed.

The mass spectra of compounds **1** and **2** did not show the molecular ion peaks; the base peak at *m*/*z* 163 is derived from the adamantoyl cation followed by next intense signal for adamantyl cation at *m*/*z* 135 is which further fragments to weaker signals at *m*/*z* = 93, 80, 79, 67, 41 and 39. The other major fragments at *m*/*z* = 180 and 179 correspond to those of the N-McLafferty rearrangement. The mass spectrum of **3** showed the molecular ion peak at *m*/*z* = 328, the other important peaks appeared at *m*/*z* 313, 222, 179, 163 (100), 135, 149. The observed fragmentation pattern is in agreement with the mass spectra study reported by Martínez-Alvarez et al. [34] on a series of acylthiourea species, which the main fragment is produced by α-cleavage to the carbonyl group to form a well-stabilized acylium cation.

Further characterization includes the X-ray diffraction analysis and the vibrational spectra (including infrared and Raman) discussed in the following sections.

3.2. X-ray crystal structure

Compounds **1** and **3** crystallize with each two independent molecules per asymmetric unit, denoted A and B. All cyclohexane rings adopt a chair conformation. The dihedral angle between the best plane through the thiourea moiety OCNCSN and the phenyl plane measures 47.21(5)° and 45.06(5)° for molecules A and B of **1** and 30.72(4)° for **2**. The molecular conformations of **1** and **2** are stabilized by intra-molecular N—H···O hydrogen bonds forming six-membered rings. On the other hand, molecules of **3** are strongly



1; R_1= 3-$NO_2C_6H_4$, R_2= H
2; R_1= 3-$NO_2C_6H_4$, R_2= H
3; R_1= C_6H_5, R_2= CH_3

Scheme 1. Synthesis of 1-(adamantane-1-carbonyl)-3-substituted thioureas.

twisted with torsion angles S—Cx12—Nx01—Cx01 of 126.8(2)° (x = 1 for A) and 130.6(2)° (x = 2 for B), respectively.

These conformational differences observed between compounds **1**–**2** and **3** are in agreement with the a recent article by Becker and coworkers [35] where 739 structures containing the —C(C=O)N(C=S)N— moiety found in the Cambridge Crystallographic Database were analyzed. As vastly documented for *1*-benzoyl-*3*-alkyl substituted thioureas, a local planar structure of the central —C(O)—NH—C(S)—NH— moiety is preferred, with opposite orientation between the C=O and C=S double bonds ("*S*-shape"). In this conformation the C=O and H—N groups form a pseudo 6-membered ring, favoring an intra-molecular interaction through a hydrogen bond [36]. When the formation of suitable hydrogen bond is prevented, as in 3,3-disubstituted derivatives, the anticlinal geometry, with $\varphi_{SCCO} \approx 120°$ is preferred [37]. This conformation is also referred as "*U*-shape" and found for example in 1-furoyl-3,3-disubstituted thioureas [38].

The geometrical parameters of compounds **1**–**3** around the central 1-acyl thiourea moiety derived from the X-ray analysis are listed in Table 2, together with the values for close related adamantane 1-carbonyl thiourea species, as determined previously [14]. Table 1 also contains the geometrical data available for related 1-acyl 3,3-(methyl, phenyl) di-substituted thiourea [39], which is structurally related with compound **3,** and allows to compare the effect of the 3,3-disubstitution on the nitrogen atom. Moreover, the computed parameters for the compounds here studied are also listed in Table 2. It has been reported that the B3LYP method with moderate large basis sets (6-311++G**) predicts the bond length around the thiourea group very well, including the C=S bond.

The amidic-N—C(O) and thioamidic-like bond lengths (ca. 1.38 and 1.34 Å, respectively) shows little deviation for the three compounds here studied, being shorter than C—N single bond [40], as expected from their partial double bond character [12]. On the other hand, the N(1)—C(S) connecting both groups amounts 1.383(2) and 1.386(2) Å for compounds **1** and **2**, respectively, and it is slightly longer [1.398(3) Å] for compound **3**. This observation suggest that resonance interactions are favored in the case of **1** and **2** – probably facilitated by the planar —C(O)NHC(S)NH— group [41,42]–, and disfavored in the case of the non-planar structure of **3**.

The C—N(1)—C bond angle of compounds **1** and **2** [128.6(1) and 128.8°, respectively] are very similar to that determined for the other 1-acyl-3-mono-substitued thioureas listed in Table 2 [43]. It should be noted that for compound **3** the value is significantly lower 123.8(2)°. This difference is probably related with the fact that the *S* conformation adopted by compounds **1** and **2** optimizes the intra-molecular N—H···O=C hydrogen bond. On the other hand, the N(1)—C—N(2) bond angles found for compounds **1** and **2** [115.6(1)°] are lower than that of **3** [117.5(2)°], accounting for the steric effects of the latter due to the di-substitution on the N(1).

It is worthy noticing that as is shown in Table 2, quantum chemical calculations at the B3LYP/6-311++G** reproduce the geometrical parameters in general good agreement with the experimental data for each compound, as well as the tendencies found when the three compounds are compared each other [44].

Additionally, all three crystal packings of **1**, **2** and **3** show N—H···S inter-molecular interactions that link molecules into non-crystallographic centro-symmetric dimers with H···S distances ranging from 2.55 to 2.77 Å and N—H···S angles 152° to 171°. The crystal packing pattern for **1** (Fig. 4) shows the inter-molecular N102—H···S2 and N202—H···S1 bridges that link each an A/B molecule pair forming non-crystallographic centro-symmetric dimers which are stacked along [100]. For **2** the N—H···S($-x+1$, $-y+1$, $-z$) inter-molecular bonds link molecules also to centro-symmetric dimers stacked along [010] (Fig. 5). Finally, for **3** (Fig. 6) the N102—H···S201($-x+0.5$, $y-0.5$, $-z+0.5$) and N202—H···S101($-x+0.5$, $y+0.5$, $-z+0.5$) interactions result in a similar A/B linking as for **1** but now stacked along [010]. It is worthy to notice that N—H···S=C hydrogen bonds are commonly encountered in 1-acyl-thioureas, probably due to the fact that nearly planar molecular dimeric chain are formed through centro-symmetric $R_2^2(8)$ packing motif [45].

3.3. Vibrational analysis

Taking into account the structural features determined for compounds **1**–**3**, it is interesting to analyze their infrared and Raman spectra for determining how the inter- and intra-molecular interactions affect the vibrational properties. Table 3 collects the infrared and Raman data measured for the three compounds here studied. These results are analyzed with the help of quantum chemical calculations at the B3LYP/6-311++G** level. The joint analysis of both infrared and Raman spectroscopy have showed to be appropriate for study the effect on the substitution for a series of mono- and di-substituted thioureas [38]. Moreover, the analysis includes a tentative assignment of the main bands observed in the spectra which is done by comparison with reported vibrational data available in the literature for similar molecules [41,46–56].

As listed in Table 3, strong absorptions at 3321 and 3310 cm^{-1} are found in the infrared spectra of compounds **1** and **2**, respectively, which can be associated with the ν(N(1)—H) stretching

Table 2
Experimental X-ray and calculated (B3LYP/6-311++G**) selected geometric parameters (Å and °) of the central 1-acyl-thioamide group for compounds **1**–**3**. Available geometrical parameters for related molecules are also given.

Parameter[a]	**1** Expl.[b]/calc.	**2** Expl./calc.	**3** Expl.[b]/calc.	Ref. [33][c]	Ref. [14][d]	Ref. [33][e]	Ref. [39][f]
C=O	1.222(2)/1.226	1.222(2)/1.226	1.216(2)/1.212	1.223(2)	1.211(2)	1.214(2)	1.221(2)
C=S	1.670(2)/1.668	1.671(1)/1.668	1.667(2)/1.674	1.664(2)	1.675(2)	1.658(2)	1.680(2)
C(8)—N(2)	1.387(2)/1.383	1.392(2)/1.385	1.383(2)/1.401	1.383(2)	1.377(3)	1.374(2)	1.387(2)
N(2)—C(S)	1.383(2)/1.409	1.386(2)/1.407	1.398(3)/1.408	1.390(2)	1.377(2)	1.388(2)	1.405(2)
C(1)—N(1)	1.340(2)/1.353	1.344(2)/1.355	1.347(2)/1.352	1.343(2)	1.325(3)	1.328(2)	1.343(2)
N(1)—C(Ph)	1.416(2)/1.407	1.412(2)/1.403	1.434(2)/1.442	1.407(2)	1.425(2)	1.418(2)	1.447(2)
O=C—N(2)	121.2(2)/121.9	121.0(1)/121.9	121.7(2)/122.4	121.1(1)	120.8(2)	121.8(2)	122.8(1)
(O)C—N(2)—C(S)	128.6(1)/130.7	128.8(1)/130.7	123.8(2)/125.8	128.4(2)	129.9(2)	128.4(1)	124.1(1)
N(1)—C(1)—N(2)	115.6(1)/113.5	115.6(1)/113.4	117.5(2)/116.4	114.4(1)	117.7(2)	115.6(1)	117.3(1)
C(1)—N(1)—C(Ph)	125.6(1)/132.1	128.1(1)/132.4	123.9(1)/122.8	128.0(2)	119.5(2)	123.6(1)	123.5(1)
S=C—N(1)	125.2(1)/129.3	126.1(1)/129.5	123.1(1)/124.7	126.8(1)	124.7(1)	126.5(1)	123.2(1)

[a] For atom numbering see Figs. 1–3.
[b] Mean values determined from crystallographically independent molecules.
[c] 1-(Adamantane-1-carbonyl)-3-(2,4-dichlorophenyl).
[d] 1-(Adamantan-1-ylcarbonyl)-3-(2,6-difluoro-4-hydroxyphenyl)thiourea.
[e] 1-(Adamantane-1-carbonyl)-3-(2-bromo-4,6-difluorophenyl)thiourea.
[f] 1-(3-Chlorobenzoyl)-3,3-(methyl-phenyl)thiourea.

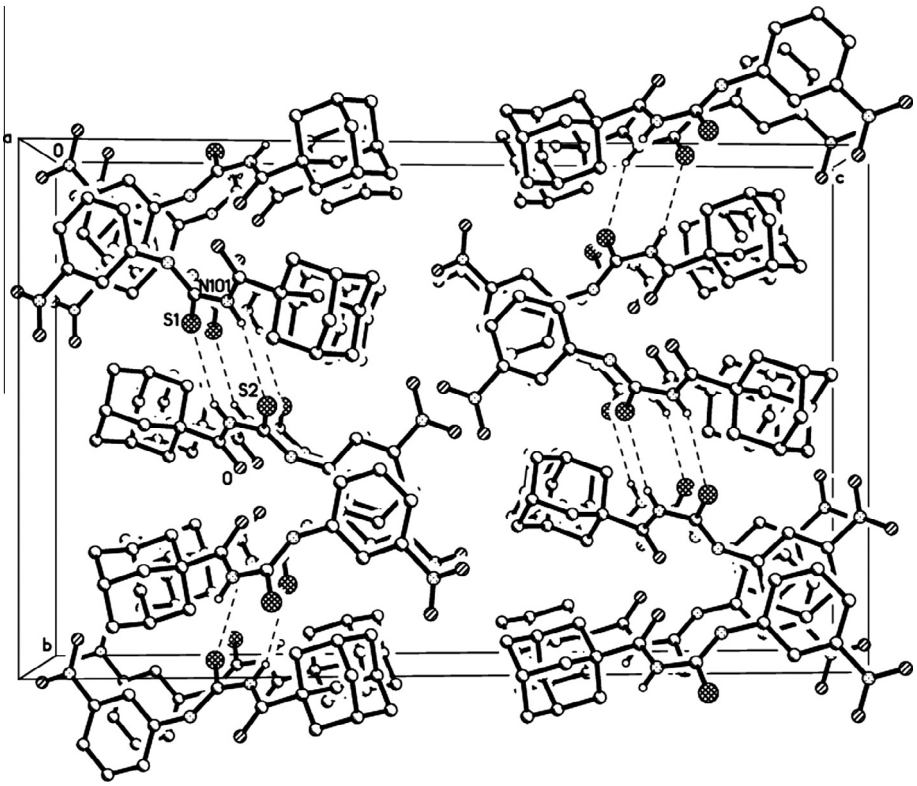


Fig. 4. Crystal packing of **1** viewed along *a*-axis with inter-molecular N—H···S pattern drawn as dotted lines. H-atoms not involved are omitted.

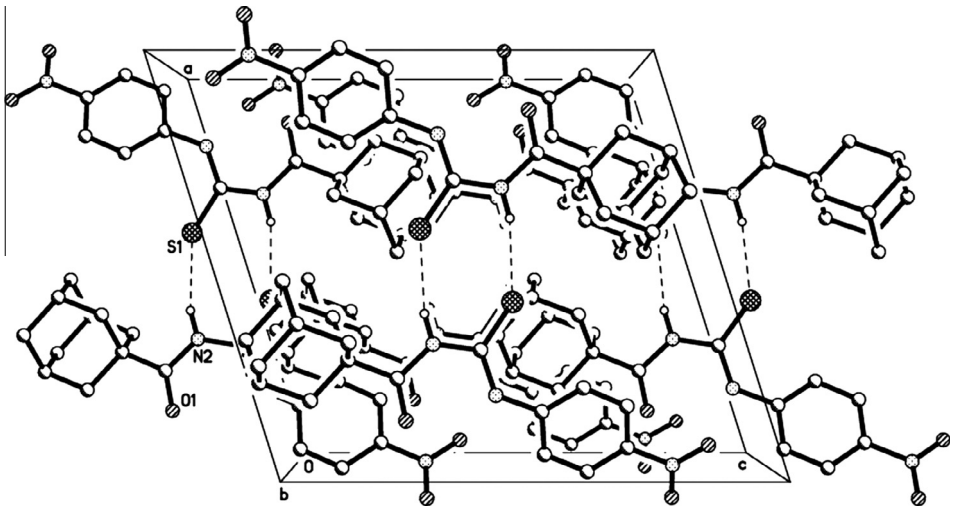


Fig. 5. Crystal packing of **2** viewed along *b*-axis with inter-molecular N—H···S pattern drawn as dotted lines. H-atoms not involved are omitted.

mode [33]. In effect, as predicted by the quantum chemical calculations, the formation of the intra-molecular N(1)—H···O=C hydrogen bond produces a red-shift and a strong intensification of the ν(N(1)—H) normal mode as compared with the other thio-amide ν(N(2)—H) stretching [57]. However, as has been also pointed out, the contribution of Fermi resonance effects with the ν(C=C) first overtone and ν(C=C) + δ(N—H) combinations modes cannot be rule out for explaining the strong intensity displayed by this absorption [58]. As expected, this feature is absent in the vibrational spectra of **3**. Several other $\nu(C—H)_{arom}$ and $\nu(C—H)_{adam}$ stretching modes can be observed in the 2800–3200 cm^{-1} region.

Fig. 7 shows the 1800–1300 cm^{-1} region of the infrared and Raman spectra of **1**–**3**, where the most important modes for the central —C(O)NHC(S)NH— skeleton are expected to appear. Singularly, the region of the ν(CO) stretching vibration is of main interest for analyzing the presence of the intra-molecular hydrogen bond [59]. As can be seen in Fig. 7, ν(CO) for **3** appears as strong absorption at 1700 cm^{-1} (1703 cm^{-1} Raman), whereas **1** and **2** species show strong infrared absorptions at 1681 and 1686 cm^{-1}, with counterparts at 1679 and 1684 cm^{-1} in the Raman spectra, respectively. Quantum chemical calculations at the B3LYP/6-311++G** level of approximation for the molecules isolated in a vacuum agree with this description, with computed ν(CO) values of 1650 and 1654 cm^{-1} for **1** and **2**, respectively, and 1693 cm^{-1} for **3**. Thus, it becomes clear that the ν(CO) red-shift of ca. 20 cm^{-1} observed for **1** and **2** respect to compound **3**, denotes

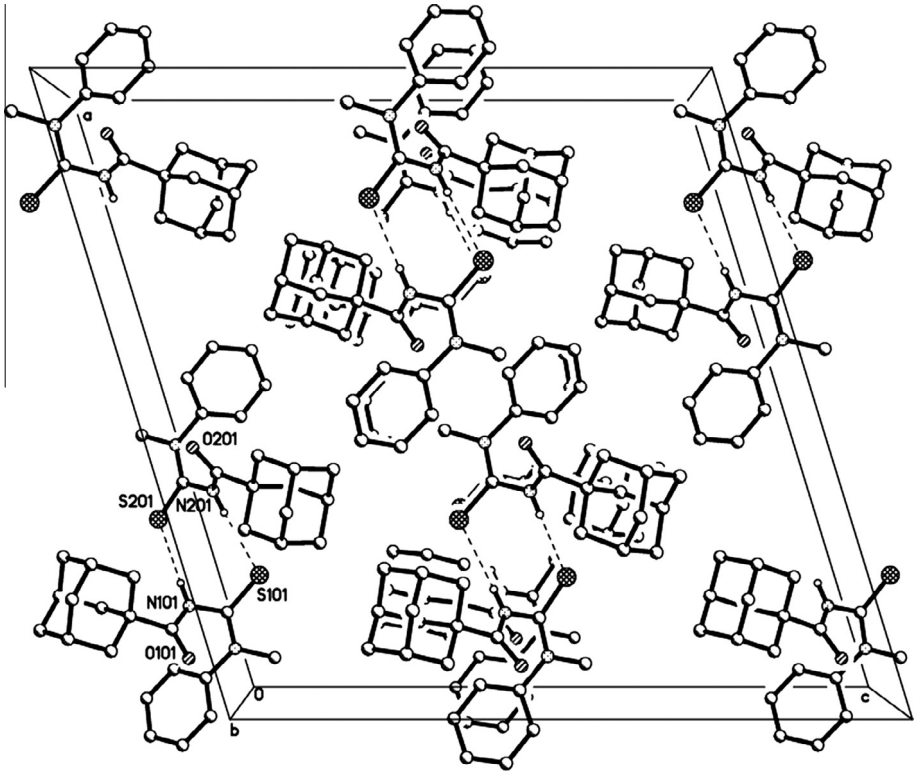


Fig. 6. Crystal packing of **3** viewed along *b*-axis with inter-molecular N—H···S pattern drawn as dotted lines. H-atoms not involved are omitted.

the influence of the N—H···O=C intra-molecular hydrogen bond in the former species.

The region between 1500 and 1600 cm^{-1}, where the δ(N—H) deformation mode (thioamide band I) appears, could also serves a signature for identify intra- and/or inter-molecular hydrogen bonds [59]. The analysis of the infrared spectra (see Fig. 7) reveals the presence of very strong and rather broad absorptions at around 1544 (1541 cm^{-1} Raman) and 1547 cm^{-1} (1550 cm^{-1} Raman) for **1** and **2**, respectively, which can be assigned to this normal mode [60]. Contributions from ν(C=C) stretching modes from the phenyl ring cannot be excluded, as also suggested by quantum chemical calculations (see the computed intensity values in Table 3). Moreover, a second superposed absorption can be determined at 1516 and 1508 cm^{-1} for **1** and **2**, respectively. Quantum chemical calculations suggest that these modes are due to the $\nu_{as}(NO_2)$ stretching. As expected, this last mode is absent in the molecule **3**. It is obvious that the thioamide band I is not expected to occurs for 3,3-substituted thioureas, thus the intense band at 1598 cm^{-1} in the Raman spectrum of compound **3** is assigned with confidence to ν(C=C) stretching modes, in agreement with previous studies [61].

The second δ(N—H) fundamental, associated with the —C=S—N—H— moiety, appears at lower wavenumbers, also as intense absorptions at 1451 (1440), 1448 (1437) and 1453 (1457) cm^{-1} for **1**, **2** and **3**, respectively (Raman shift in parenthesis). These values are in agreement with the previously reported data for related species [38,62].

The thioamide band II, mainly associated with the ν_{as}(NCN) antisymmetric stretching, is expected to occurs as a strong absorption around 1350 cm^{-1}. Reguera et al. [38] showed that this mode is sensitive to the substitution, 3,3-disubstitued thioureas appearing at higher wavenumbers (up to 1395 cm^{-1}) than that of the 3-monosubstituted ones, below 1350 cm^{-1}. In agreement with this trend, the absorptions at 1350 cm^{-1} observed in the infrared spectra of **1** and **2** are assigned to this mode, whereas for **3**, the corresponding band appears at 1376 cm^{-1}. It is plausible that both, the donating electron nature of the methyl group and the resonance effect between the nitrogen atom with the phenyl group contribute to this higher frequency for compound **3**. It should be stressed, also, that contribution of the $\nu_s(NO_2)$ symmetric stretching modes are also expected in this region for compounds **1** and **2**.

Taking into account the vibrational properties reported for the simple thiourea molecule [63], it is expected that the corresponding symmetric motion of the C—N stretching modes at around 1150 cm^{-1} [64,65]. Thus, following the quantum chemical calculation description, the ν_s(NCN) symmetric stretching modes (usually assigned as thioamide band III), are assigned to the 1153 (1146) and 1150 (1143) cm^{-1} intense absorptions found in the infrared spectra of **1** and **2** and to the 1176 cm^{-1} (1171 cm^{-1}) band for **3** (Raman values are given in parentheses). Again, a slightly higher frequency value is observed for compound **3**, probably associated with electronic contributions from the 3,3-methyl-phenyl substituents through inductive and resonance interactions.

The adamantyl group is responsible for the very strong band observed in the Raman spectrum at 766, 771 and 769 cm^{-1} for **1**–**3**, respectively, which can be assigned with confidence to the "breathing mode", in agreement with the Raman spectra observed for adamantane isotopomers [66].

For the parent the thiourea molecule, the ν(C=S) stretching mode is reported at 1094 cm^{-1} in the infrared spectrum (1105 cm^{-1} Raman) [63]. However, as has already been pointed out [62], lower values were found for this mode (also named as the thioamide band IV) in substituted thiourea derivatives, typically in the 600–800 cm^{-1} range [3,38,61,67]. This strong variation is an indication that the frequency of the ν(C=S) stretching mode is very sensitive to the presence of inter-molecular interactions involving the C=S group [46]. Moreover, it is expected that the polarizability of the C=S bond originates an intense Raman dispersion [68]. Based on these considerations, we tentatively assigned

Table 3
FTIR and FT-Raman experimental data (in cm^{-1}) for compounds **1**–**3**, together with the computed B3LYP/6-311++G** values and tentative normal mode assignment.

1			**2**			**3**			Tentative assignment[c]
FTIR[a]	Raman[a]	Calculated[b]	FTIR[a]	Raman[a]	Calculated[b]	FTIR[a]	Raman[a]	Calculated[b]	
		3463 (8.1)			3467 (6.4)			3459 (7.4)	ν(N(2)—H)
3321 s		3187 (84.2)	3310 m		3178 (67.2)				ν(N(1)—H)
3111 m		3115 (5.3)	2927 sh	3082 vw	3111 (1.5)	3160 br		3065 (2.3)	$\nu(C—H)_{arom}$
3093 m	3096 vw	3077 (6.2)	2909 m	2951	2931 (17.8)	3075 w	3077 w	3058 (4.3)	
2930 w	2923 vs	2954 (10.0)	2894 w,sh	vw,sh	2929 (5.0)	2926 sh	2948 w,sh	3048 (5.8)	
2908 w	2909 s,sh	2955 (7.1)		2921 s		2906 m	2915 s		
				2896 w,sh					
2853 m	2853 s	2930 (23.5)	2849 m	2852 m	2916 (9.9)	2848 m	2849 m	2957 (6.9)	$\nu(C—H)_{adam}$
		2929 (7.3)			2913 (14.1)			2933 (12.7)	
								2929 (6.3)	
								2927 (28.1)	
								2908 (26.8)	
1681 m	1679 m	1650 (26.1)	1686 m	1684 w	1654 (16.8)	1700 s	1703 m	1693 (46.4)	νC═O
	1616 m	1584 (86.6)	1605 m		1592 (46.0)	1596 w	1598 s	1572 (2.6)	νC═C
					1572 (21.4)				
1593 sh	1592 s	1542 (100)		1601 s	1557 (93.2)				νC═C
1544 br	1541 m,br	1524 (50.2)	1547 s	1550 m,br	1504 (28.5)				δ(N—H) Thioamide band I
1516, s	1522 w	1482 (86.4)	1508 vs br	1515 m	1481 (62.9)				$\nu_{as}NO_2$/νC═C
				1493 m	1464 (17.6)				
						1508 vs br	1509, vvw		νC═C
							1521 m, br		
1451 m	1440 s	1451 (14.1)	1448 s, sh	1437 m	1456 (2.7)	1453 m	1457 w	1482 (100)	δ(N—H)
						1435 s	1446 vw 1436 m	1462 (5.0)	$\delta_s(CH_3)$
								1403 (32.1)	
1350 s	1351 vs	1326 (12.3)	1350 m	1347 vs	1308 (23.9)	1376 vs	1376 m	1333 (88.3)	ν_{as}(NCN) Thioamide band II
1319 m, br	1318 w	1312 (89.3)	1344 m	1333 sh	1292 (45.5)				$\nu_s(NO_2)$
1286 m	1286 vvw	1297 (27.5)	1321 m	1300 m	1280 (100)	1320 w	1321 vw	1286 (2.3)	$\delta(C—H)_{adam}$
		1284 (40.5)	1299 s	1256 m	1278 (42.3)	1296 w	1298 w	1270 (4.8)	
1255 m	1255 s	1256 (4.5)	1258 m		1224 (13.2)	1282 m	1277 w	1246 (30.1)	
						1266 m	1257 w	1236 (5.6)	
1215 m	1213 w	1216 (8.7)	1211 m	1210 w	1178 (4.5)	1224 s	1224 w	1177 (19.1)	$\nu_{as}(NC)_{arom}$
	1189 w		1184 w	1187 m,br	1158 (4.6)	1184 s	1184 m	1146 (26.0)	$\delta(C—H)_{adam}$
1179 w	1178 w	1144 (10.1)	1176 w		1147 (11.4)				$\delta(C—H)_{adam}$
1153 vs	1146 m	1109 (50.8)	1150 m	1143 vw	1111 (34.1)	1176 m	1171 w	1138 (27.3)	ν_s(NCN) Thioamide band III
						1118 s	1120 vw	1093 (20.6)	$\nu(N—CH_3)$
						1106 s, br	1104 m, br	1091 (13.5)	$\delta_{as}(CH_3)$
								1078 (7.5)	
1099 m, br	1102 m, br	1056 (12.6)	1101 w		1077 (22.6)	1076 w	1058 vw	1053 (1.8)	$\nu(C—C)_{adam}$
						1060 m		1026 (8.2)	
1061 m	1062 vw	1036 (2.0)	1062 m	1061 vw	1036 (2.8)	1025 m	1025 m	1003 (2.0)	$\delta(C—H)_{adam}$
1045 w,br	1045 vvw	1010 (1.6)	977 w	1014 vw	951 (2.5)	1005 w	1006 s	978 (0.8)	
1001 vw	1002 s	973 (1.0)							
976 w	979 m	957 (2.0)		977 vw		974 w	977 m	950 (2.1)	
936 w	939 w	907 (1.9)	952 w	939	946 (0.7)	938 w	937 w	942 (1.2)	$\nu(C—C)_{adam}$
914 w	914 w	889 (1.4)		vw,br		921 m	922 w	897 (2.5)	
889 m	889 m	845 (7.1)	896 w	897 m	871 (2.4)	871 w	870 m	846 (0.8)	ν(C═S) Thioamide band IV
869 m	867 w	803 (11.7)	860 m	859 m	835 (10.1)	837 vw	800 vw	814 (0.6)	$\rho(C—H)_{adam}$
809 m	811 m	784 (3.6)	852 s	814 w	837 (8.3)				
			813 vw		821 (3.1)	800 s		776 (3.6)	
					784 (0.7)				
774 w	766 s	748 (1.4)	773 w, br	771 m	777 (0.4)	763 s	769 vs	751 (3.9)	Breathing
									$\nu_s(C—C)_{adam}$
746 m	753 vw	727 (1.4)	756 w		741 (0.8)				$\rho(C—H)_{arom}$
736 m	738 vw	706 (3.8)	739 m	738 w	723 (3.3)	725 w	707 vw	704 (1.0)	$\nu(C—C)_{adam}$
			721 w	720 w,br	701 (0.7)	708 m		691 (5.1)	
690 m	690 m	663 (5.7)	695 w	693 vw	669 (1.6)	698 s	671 s	679 (8.2)	$\rho(C—H)_{arom}$
673 m	674 w	653 (2.6)	678 w	677 sh	647 (1.6)	670 m	645 vw	625 (7.1)	
664 m	663 w	633 (0.6)	665 w	668 m,br	638 (0.4)	647 sh		607 (0.8)	
642 w, sh	640 w	628 (0.4)	627 w	629 w	613 (0.7)	621 w	623 m	596 (6.6)	$\delta(C—C)_{arom}$
607 m	611 m, br	613 (7.7)	613 m	615 m	610 (5.1)	591 w	593 vw	571 (1.3)	
567 vw	566 vw	523 (0.8)	567 vw	569 vw	549 (1.0)				δNO_2
524 m	520 vw	503 (6.3)	493 w	493 vw	480 (1.8)	547 m	548 w	535 (6.4)	$\delta(C—C)_{adam}$
	482 vw	479	434 w			489 vw	488 vw	485 (0.5)	
	444 w	445					441 vw	453 (0.6)	
	421 vw	421		413 w	430		335 w	336	δ(NC═O)
	405 vw	410					320 m	308	δ(CNC)
	381 vw	380		382 w	381				δ(NC═S)
	331 w	336		325 w	341				$\delta(C—C)_{adam}$
	271 m	268							$\delta(C—C)_{adam}$

(*continued on next page*)

Table 3 (*continued*)

1			2			3			Tentative assignment[c]
FTIR[a]	Raman[a]	Calculated[b]	FTIR[a]	Raman[a]	Calculated[b]	FTIR[a]	Raman[a]	Calculated[b]	
	247 w	241					296 w		δ(C—C)$_{adam}$
	223 w	218					250 vw		τ
	202 w,sh	196		203 vw	206		215 m		τ
	190 vw	180					170 w		τ
	146 m	169							τ
	127 s	126							τ

[a] Solid samples as KBr pellets (FTIR), and powders (Raman). Band intensities and shape: vs = very strong; s = strong; m = medium; w = weak; vw = very weak, sh: shoulder, br: broad.

[b] Scaled computed frequency and intensity values at the B3LYP/6-311++G** level of approximation. In parentheses relative band strengths, IR relative intensities [100% ≡ 494, 674 and 392 km/mol for compounds **1**, **2** and **3**, respectively]. The computed Raman spectra are given as Supplementary material in Fig. S2.

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

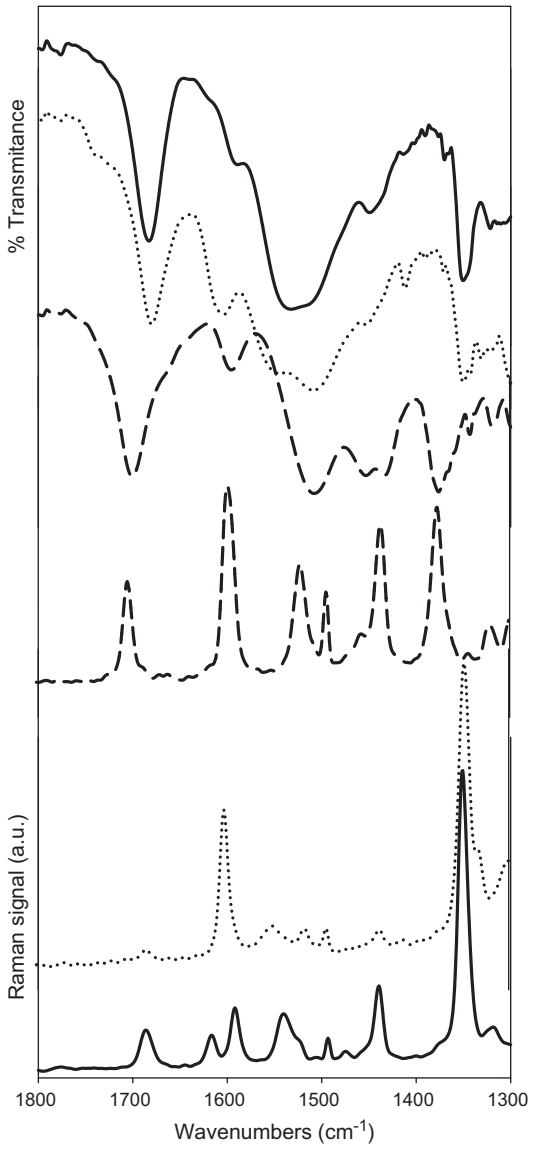


Fig. 7. FT-Raman and FTIR spectra for compounds **1** (solid line), **2** (dotted line) and **3** (dashed line) in the 1800–1300 cm^{-1} region.

the ν(C═S) mode to the medium to weak absorptions observed at 889, 896 and 871 cm^{-1}, with stronger counterparts in the Raman spectra at 889, 897 and 870 cm^{-1}, for compounds **1**–**3**, respectively.

4. Conclusion

Structural properties of three novel 1-(adamantane-1-carbonyl) thiourea derivatives (**1**–**3**) were determined by using single crystal X-ray diffraction analysis. The X-ray molecular structure is similar for compounds **1** and **2**, with the central —C(O)NHC(S)NH— moiety adopting a nearly planar structure with the C═O and C═S double bond oriented toward opposite directions ("*S*-shape"). This conformation is favored by a strong C═O···H—N intra-molecular hydrogen bond forming a (pseudo)six-membered ring. This structural motif is not present in compound **3** because the di-substitution prevents the formation of intra-molecular hydrogen bond. For compound **3** the non-planar "*U*-shape" conformation is adopted. The effects on the vibrational properties have been analyzed by using infrared and Raman spectroscopies. A clear ν(CO) red-shift of ca. 20 cm^{-1} observed for **1** and **2** respect to compound **3**, denoting the influence of the N—H···O═C intra-molecular hydrogen bond. The characteristic thioamide band II [ν_{as}(NCN)] and thioamide band III [ν_{s}(NCN)] showed a small but clear shift toward higher frequencies for compound **3**, indicating the electronic effects exerted by the methyl (inductive) and phenyl (resonance) substitutions.

Acknowledgments

MFE is member 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.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.03.002.

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