



Vibrational spectra and molecular structure of isomeric 1-(adamantan-1-ylcarbonyl)-3-(dichlorophenyl)thioureas

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ABSTRACT

1-(adamantan-1-ylcarbonyl)-3-(2,3-dichlorophenyl)thiourea, **1**, and 1-(adamantan-1-ylcarbonyl)-3-(2,5-dichlorophenyl)thiourea, **2**, were synthesized in reasonable yields from admanantyl-1-carbonyl chloride and ammonium thiocyanate followed by treatment of the resulting adamantane-1-carbonylisothiocyanate with the 2,3- and 2,5-dichloroanilines. A complete vibrational analysis was performed on the basis of FTIR and Raman spectra. The formation of intramolecular N–H···O and intermolecular N–H···S hydrogen bonds in the solids affect vibrational modes, with low frequency values observed for the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{S})$ stretching modes. Structural data obtained by single-crystal X-ray diffraction at low temperature confirm this picture. Compound **1** crystallizes in the triclinic system and compound **2** crystallizes with two unique molecules in the asymmetric unit of the orthorhombic unit cell. The molecular structures reveal that the carbonylthiourea units in **1** and both molecules of **2** are planar due in part to the formation of intramolecular N–H···O=C hydrogen bonds that generate S (6) rings. Moreover, the crystal structures are stabilized by an extensive series of classical and non-classical hydrogen bonds and, in the case of **1** by an intermolecular Cl···Cl halogen bond.

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1. Introduction

Adamantane derivatives have been of great pharmaceutical interest since the discovery of the anti-viral properties of the amino derivative, amantadine [1]. Other mainly amino or amide derivatives have found applications as antiviral agents targeting influenza [2], herpes virus [3], in the treatment of type 2 diabetes [4,5], and also of Alzheimer's disease [6]. More recently, adamantane derivatives have also appeared in the darker side of the pharmaceutical industry with the discovery that adamantan-1-yl (1-pentyl-1H-indol-3-yl)methanone (AB-001) and N-(adamantan-1-yl)-1-pentyl-1H-indole-3-carboxamide (SDB-001) were being used as components of designer drugs sold as “legal” alternatives to marijuana [7].

Carbonyl thiourea derivatives [8] are also well known for their applications as pesticides [9–11] and for their anti-tumor [12], antimicrobial [13], and antifungal [14] properties. We became interested in new materials containing both -adamantane and acyl thiourea-groups in a unique molecule, which may result in synergies to enhance their pharmaceutical potential.

From the molecular structure point of view, a search of the Cambridge Structural Database [15] for other adamantan-1-ylcarbonyl-thiourea derivatives reveals four similar compounds, that have been structurally characterized [16–19]. Adamantane carboxamide derivatives are slightly more plentiful with 15 unique organic entries in addition to the carbonyl thiourea derivatives mentioned previously [20–34]. Vibrational studies of this series of compounds have been limited to a few examples recently appeared in the specialized literature [17,18].

Herein we report the preparation, characterization, and crystal structure of isomeric 1-(adamantan-1-ylcarbonyl)-3-(di-chlorophenyl) thioureas, with 2,3- (compound **1**) and 2,5- (compound **2**) dichlorophenyl substitution. Moreover, the vibrational properties of the novel species have been analyzed by a combined

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experimental (including infrared and Raman spectroscopy) and theoretical calculations at the B3LYP/6–311++G (d,p) level of approximation.

2. Experimental

2.1. General instrumentation

Melting points were recorded using a digital Gallenkamp (SANYO) model MPD. BM 3.5 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined in CDCl_3 at 300 MHz and 75.5 MHz, respectively, using a Bruker spectrophotometer. FTIR spectra were recorded on an FTS 3000 MX spectrophotometer. Mass Spectra (EI, 70eV) on a GC-MS instrument Agilent technologies, and elemental analyses were conducted using a LECO-183 CHNS analyzer. Thin layer chromatography (TLC) was conducted on 0.25 mm silica gel plates (60 F254, Merck). Visualization was achieved with ultraviolet light. Reagents were obtained commercially and used as received.

2.2. Synthesis of 1-(adamantan-1-ylcarbonyl)-3-(isomeric dichlorophenyl)thioureas, general procedure

Adamantane-1-isothiocyanate was freshly prepared by treating a solution of adamantane-1-carbonyl chloride (10 mmol) in dry acetone (50 ml) with ammonium thiocyanate (10 mmol) in acetone (30 ml). A solution of the 2,3- or 2,5-dichloroaniline (10 mmol) in acetone (10 ml) was added and the resulting mixture stirred for 6 h. On completion (TLC control), the reaction mixture was poured into cold water and the precipitated thioureas were recrystallized by slow evaporation from chloroform-ethyl acetate (3:1).

1-(Adamantan-1-ylcarbonyl)-3-(2,3-dichlorophenyl)thiourea (1); yield 68%, mp 196 °C. FT-IR ($\nu \text{ cm}^{-1}$): 3385 (νNH), 2923, 2895, 2850 (CH_2 , CH), 1682 ($\nu\text{C}=\text{O}$), 1578, 1512 (δNH), 1325, 1310, 1218, 1160, 744 ($\nu\text{C}=\text{S}$). ^1H NMR (300 MHz, CDCl_3): δ 12.71 (br s, 1H, NH, D_2O exchangeable); 8.73 (br s, 1H, NH, D_2O exchangeable); 8.03 (d, 1H, $J = 8.6 \text{ Hz}$ Ar), 7.96 (m, 1H, Ar), 7.90 (m, 1H, Ar), 2.1 (brs, 3H, adamantane-CH), 2.03 (s, 6H, adamantane- CH_2), 1.81 (q, 6H, adamantane- CH_2 , $J = 8.6 \text{ Hz}$); ^{13}C NMR (75 MHz, CDCl_3): 178.4 ($\text{C}=\text{S}$); 171.6 ($\text{C}=\text{O}$); 134.1 (Ar), 128.6, 126.9, 125.3, 123.6, 121.6 (ArCs), 41.9, 39.2, 38.6, 36.1, 36.0, 31.6, 28.0, 27.8, (adamantane-Cs); Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{N}_2\text{OS}$ (383.34): C, 56.40; H, 5.26; N, 7.31; S, 8.36%; Found: C, 56.41; H, 5.22; N, 7.32; S, 8.31%.

1-(Adamantan-1-ylcarbonyl)-3-(2,5-dichlorophenyl)thiourea (2) yield 72%, mp 193 °C. FT-IR ($\nu \text{ cm}^{-1}$): 3353 (νNH), 2918 ($\nu\text{Ar-CH}$), 2907, 2894 (CH_2 , CH), 1681 ($\nu\text{C}=\text{O}$), 1579, 1546 (δNH), 1261, 1163, 742 ($\nu\text{C}=\text{S}$). ^1H NMR (300 MHz, CDCl_3): δ 12.7 (br s, 1H, NH, D_2O exchangeable); 8.71 (br s, 1H, NH, D_2O exchangeable); 7.89 (s, 1H, Ar), 7.56 (d, 1H, $J = 8.6 \text{ Hz}$ Ar), 7.43 (d, 1H, $J = 8.6 \text{ Hz}$ Ar), 2.1 (brs, 3H, adamantane-CH), 2.03 (s, 6H, adamantane- CH_2), 1.80 (q, 6H, adamantane- CH_2 , $J = 8.6 \text{ Hz}$); ^{13}C NMR (75 MHz, CDCl_3): 179.1 ($\text{C}=\text{S}$); 175.3 ($\text{C}=\text{O}$); 134.1 (Ar), 181.7, 128.6, 124.2, 119.7, 114.9 (ArCs), 41.9, 41.9, 39.2, 38.6, 36.1, 36.0, 31.6, 28.0, 27.8, (adamantane-Cs); Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{N}_2\text{OS}$ (383.34): C, 56.40; H, 5.26; N, 7.31; S, 8.36%; Found: C, 56.37; H, 5.20; N, 7.29; S, 8.39%.

2.3. 3-X-ray structure determination

The X-ray measurements on single crystals of **1** and **2** were carried out on an Agilent Duo diffractometer using CuK_α radiation ($\lambda = 0.71073 \text{ \AA}$) with data collection, reduction and absorption corrections controlled using CrysAlisPro [35] with data collected at 100 (2) K. Data were reduced and multi-scan absorption corrections were applied using CrysAlisPro [35]. The structures were solved by direct methods with SHELXS-97 [36] and refined using full-matrix

least-squares procedures (SHELXL-2014/7 [37] and Titan2000 [38]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms bound to carbon were placed in the calculated positions, and their thermal parameters were refined isotropically with $U_{\text{eq}} = 1.2\text{--}1.5 U_{\text{eq}}(\text{C})$. The N–H hydrogen atoms were located in difference Fourier maps and their coordinates were refined with $U_{\text{eq}} = 1.2 U_{\text{eq}}(\text{N})$. Compound **2** crystallized with two unique in the unit cell. The numbering scheme for compound **2** labels atoms with a leading 1 or 2 as appropriate. All molecular plots and packing diagrams were drawn using Mercury [39] and additional metrical data were calculated using PLATON [40]. Details of the X-ray measurements and crystal data for all of the complexes are given in Table 1.

2.4. Vibrational spectroscopy

Solid-phase (in KBr pellets) infrared spectra were recorded with a resolution of 2 cm^{-1} in the $4000\text{--}400 \text{ cm}^{-1}$ range on a Bruker EQUINOX 55 FTIR spectrometer. Raman spectra for compounds **1** and **2** were recorded using a Horiba Jobin Yvon T64000 Raman spectrometer equipped with a liquid N_2 -cooled back-thinned CCD detector. Spectra were recorded as the co-addition of up to 16 individual spectra with CCD exposure times of 10–20s each.

2.5. Computational details

Molecular quantum chemical calculations were performed by using the B3LYP DFT hybrid methods as implemented in the GAUSSIAN 03 program package [41]. The valence triple- ξ basis set augmented with diffuse and polarization functions in both the hydrogen and heavy atoms [6–311++G (d,p)] has been used for geometry optimization and frequency calculations. The X-ray structure was used as the initial geometry and fully optimized. The computed structures corresponded in all cases to potential energy minima for which no imaginary frequencies were found.

3. Results and discussion

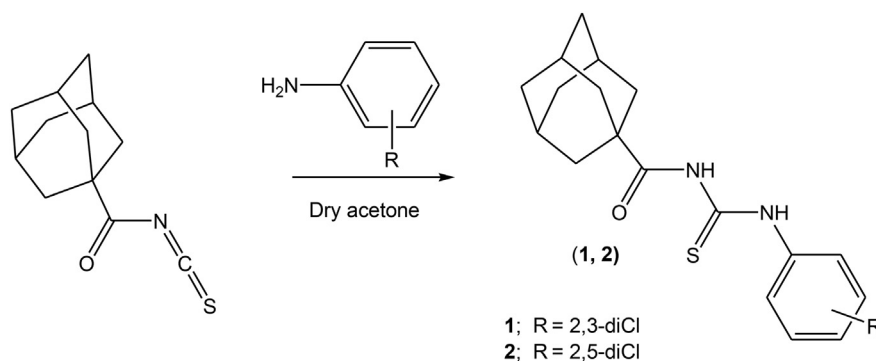
3.1. Synthesis and characterization

The isomeric 1-(adamantan-1-ylcarbonyl)-3-(dichlorophenyl) thioureas were synthesized using a one-pot method by modification of the route previously reported by us [17] (Scheme 1). Accordingly adamantane-1-carbonyl isothiocyanate was freshly prepared by reaction of adamantane-1-carbonyl chloride with an equimolar quantity of ammonium thiocyanate in dry acetone. This solution was treated individually with an equimolar quantity of 2,3- and 2,5-dichloroaniline in acetone to furnish the thiourea derivatives **1** and **2**, respectively.

In the ^1H NMR the characteristic signals of adamantyl moiety appeared as 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 for HN(1) and HN(2) respectively. In the ^{13}C NMR the characteristic adamantyl signals were observed at δ 27.7, 36.1–36.4, 38.6–38.5 and 41.5 and around δ 179 and δ 175 ppm for carbonyl and thiocarbonyl respectively. The FTIR spectra of adamantyl thioureas **1** and **2** show intense and characteristic absorptions at 3352, 3125 (free and associated NH), 3024 (Ar-CH), 2926 (CH_2), 2850 (CH), at 1672–1685 and ca. 740 cm^{-1} for carbonyl and thiocarbonyl, respectively (vibrational properties are discussed in details below).

Table 1
Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	C ₁₈ H ₂₀ Cl ₂ N ₂ OS	C ₁₈ H ₂₀ Cl ₂ N ₂ OS
Formula weight	383.32	383.32
Temperature (K)	100 (2)	100 (2)
Crystal system	Triclinic	Orthorhombic
Space group	P $\bar{1}$	P 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions		
a (Å)	6.7936 (2)	6.4252 (2)
b (Å)	10.3125 (3)	18.3151 (6)
c (Å)	12.8879 (4)	29.3226 (10)
α°	103.973 (2)	90
β°	92.063 (2)	90
γ°	94.913 (3)	90
Volume (Å ³)	871.48 (5)	3450.6 (2)
Z	2	8
Dc (Mg/m ³)	1.461	1.476
Absorption coefficient (mm ⁻¹)	4.528	4.574
F (000)	400	1600
Crystal size (mm ³)	0.23 × 0.18 × 0.08	0.23 × 0.18 × 0.13
Wavelength (Å)	1.54184	1.54184
Theta range for data collection (°)	3.540 to 74.404	3.862 to 75.208
h	−8 ≤ h ≤ 8	−7 ≤ h ≤ 5
k	−12 ≤ k ≤ 12	−22 ≤ k ≤ 22
l	−16 ≤ l ≤ 16	−36 ≤ l ≤ 36
Reflections collected	16434	18413
Independent reflections	3478	6709
R (int)	0.0489	0.0786
Completeness to theta = 67.684°	99.8%	99.8%
Max. and min. transmission	1.0000/0.5107	1.0000/0.7697
Data/restraints/parameters	3478/0/223	6709/0/445
Goodness-of-fit on F ²	1.056	1.034
Final R indices [I > 2sigma(I)]	R1 = 0.0394, wR2 = 0.1012	R1 = 0.0700, wR2 = 0.1588
R indices (all data)	R1 = 0.0452, wR2 = 0.1077	R1 = 0.0838, wR2 = 0.1677
max/min ΔF (e.Å ⁻³)	0.483 and −0.252	0.834 and −0.701

**Scheme 1.** Synthetic pathway to isomeric 1-(adamantan-1-ylcarbonyl)-3-(dichlorophenyl)thioureas.

3.2. X-ray crystal structures

The structure of **1** is shown in Fig. 1(a) with that of compound **2**, which crystallizes with two discrete molecules, **2** (1) and **2** (2), in the asymmetric unit, in Fig. 1(b). The two molecules of **2** differ markedly in the orientation of the carbonylthiourea and the 2,5-dichlorophenyl groups of the molecules, with dihedral angles between the benzene ring planes and the C(O)NC(S)N meanplanes of 40.3 (2)° for molecule **2** (1) and 64.3 (2)° for molecule **2** (2). The compounds are sufficiently similar for their molecular structures to be discussed together, each comprising an adamantane unit linked to the carbonyl carbon atoms of the carbonylthiourea moieties. These in turn carry dichlorophenyl substituents (2,3- for **1** and 2,5- for **2**) on the N1, N11 and N21 atoms of the thiourea units. Intra-molecular N1–H1N...O8, N11–H11...O18 and N21–H21...O28 hydrogen bonds form S (6) rings [42] and contribute to the relative

planarity of the carbonylthiourea moieties which have an rms deviations of 0.0586 Å for **1**, 0.0745 Å for **2** (1) and 0.0727 Å for **2** (2) from their respective C(O)NC(S)N meanplanes. The adamantane units are nicely ordered in all three molecules with the four six-membered rings that comprise the adamantane skeleton adopting chair conformations in each case.

The geometrical parameters around the central acylthiourea moiety are listed in Table 2, together with the computed [B3LYP/6–311++G (d,p)] values. The agreement between the computed and experimental geometrical parameters is very good, with a maximum error of 0.025 Å and 3.3°, for the C (7)–N (2) bond length and C (7)–N (1)–C (1) bond angle, respectively.

In the crystal structure of **1** pairs of N2–H2N...S7 hydrogen bonds, Table 3, generate inversion dimers with an R₂² (8) ring motif [42]. Weaker C17–H17A ... S7 contacts support each of these hydrogen bonds and form R₂¹ (7) rings [42]. They further

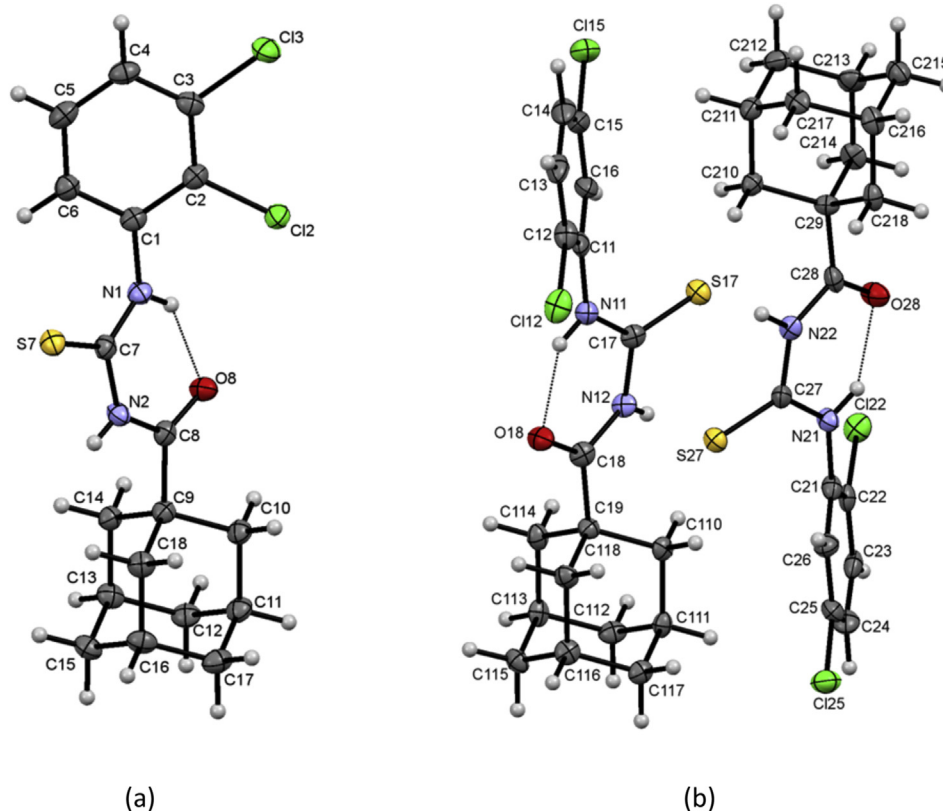


Fig. 1. (a) The molecular structure of **1**. (b) The two unique molecules of **2**. Ellipsoids are drawn at the 50% probability level and intramolecular hydrogen bonds are drawn as dotted lines.

Table 2

Selected bond lengths [Å] and angles [°] for **1** and **2**. Computed values at the B3LYP/6–311++G (d,p) level of approximation.

	1	1 (calc)	2 (mol 1)	2 (mol 2)	2 (calc)
C (1)–N (1)	1.416 (3)	1.424	1.414 (10)	1.399 (10)	1.409
C (2)–Cl (2)	1.727 (2)	1.741	1.731 (9)	1.736 (8)	1.755
C (3)–Cl (3) (5)	1.735 (2)	1.747	1.752 (9)	1.374 (11)	1.755
N (1)–C (7)	1.340 (3)	1.347	1.358 (10)	1.360 (10)	1.352
C (7)–N (2)	1.388 (3)	1.405	1.382 (9)	1.382 (9)	1.407
C (7)–S (7)	1.669 (2)	1.668	1.653 (8)	1.660 (8)	1.671
N (2)–C (8)	1.378 (3)	1.381	1.373 (10)	1.388 (9)	1.382
C (8)–O (8)	1.221 (2)	1.226	1.220 (10)	1.220 (10)	1.226
C (8)–C (9)	1.528 (3)	1.533	1.526 (10)	1.526 (10)	1.532
C (7)–N (1)–C (1)	126.22 (17)	123.9	127.0 (7)	125.5 (7)	128.8
N (1)–C (7)–N (2)	114.76 (18)	114.9	113.3 (7)	114.0 (6)	114.2
N (1)–C (7)–S (7)	127.19 (15)	126.3	126.2 (6)	126.7 (6)	128.6
N (2)–C (7)–S (7)	118.01 (16)	118.8	120.3 (6)	119.2 (6)	117.2
O (8)–C (8)–N (2)	121.85 (18)	122.1	120.9 (7)	121.9 (7)	122.0
O (8)–C (8)–C (9)	121.87 (17)	120.8	121.2 (7)	121.7 (7)	121.1

encapsulate the N–H...S dimers into larger R_2^2 (14) rings [42]. On the obverse sides of these dimers, Cl ... Clⁱ contacts (3.4242 (7) Å; $i = -x+3, -y+2, -z+2$) [43] link the Cl2 and Cl3 substituents on adjacent dichlorophenyl rings to construct a second form of inversion dimer. The net result of these contacts is to link the molecules into infinite sheets approximately parallel to the (1, -2, 2) plane, as shown in Fig. 2. Molecules are further linked head to tail by C16–H16A ... Cg1 contacts [44], Table 3, to form yet another inversion dimer, Fig. 3, and complete the intermolecular contacts observed in the packing of this molecule. This series of intermolecular contacts combine to stack molecules along a axis Fig. 4.

Table 3

Hydrogen bonds for **1** and **2** [Å and °].

D–H...A	d (D–H)	d (H ... A)	d (D ... A)	∠(DHA)
Compound 1				
N (1)–H (1 N) ... O (8)	0.83 (3)	1.94 (3)	2.629 (2)	140 (2)
N (2)–H (2 N) ... S (7) ⁱⁱ	0.76 (3)	2.92 (3)	3.4445 (19)	128 (2)
C (14)–H (14 A) ... S (7) ⁱⁱ	0.99	2.91	3.841 (2)	158
C (18)–H (18 A) ... Cg (1) ⁱⁱⁱ	0.99	2.92	3.735 (2)	140
Compound 2				
N (11)–H (11) ... O (18)	0.85 (9)	1.87 (9)	2.599 (9)	143 (9)
N (21)–H (21) ... O (28)	0.86 (9)	1.86 (9)	2.599 (8)	142 (8)
N (12)–H (12) ... S (27) ^{iv}	0.73 (9)	2.83 (10)	3.487 (7)	150 (9)
C (110)–H (11G) ... S (27) ^{iv}	0.99	2.78	3.718 (8)	158
N (22)–H (22) ... S (17) ^{iv}	0.93 (9)	2.66 (9)	3.468 (7)	146 (7)
C (218)–H (21G) ... S (17) ^v	0.99	2.88	3.790 (8)	153
C (210)–H (21J) ... S (17) ^v	0.99	2.82	3.742 (9)	155
C (13)–H (13) ... Cg (3) ^{vi}	0.95	2.90	3.567 (9)	129
C (110)–H (11H) ... Cg (3) ^{vii}	0.99	2.80	3.516 (8)	130
C (23)–H (23) ... Cg (2) ^{viii}	0.95	2.86	3.562 (9)	131
C (210)–H (21I) ... Cg (2) ^{ix}	0.99	2.89	3.563 (8)	126

Symmetry operations: ii = $-x+1, -y+1, -z+2$; iii = $-x+2, -y+1, -z+2$; iv = $-x+1, y+1/2, -z+3/2$; v = $-x+1, y-1/2, -z+3/2$; vi = $x, y+1, z$; vii = $x+1/2, -y+1/2, -z+1$; viii = $x-1, y-1, z$; ix = $x+1/2, -y-1/2, -z+1$.

Intermolecular N–H...S contacts also feature in the packing of **2** but in this case R_2^2 (8) dimers [42] form via N12–H12...S27 and N22H22...S17 hydrogen bonds linking adjacent **2** (1) and **2** (2) molecules. The N12–H12...S27 contacts are supported by two C–H...S17 contacts generating an R_1^1 (6) and two R_1^1 (7) rings [42]. The alternate N12–H12...S27 hydrogen bond is bolstered by a single C110–H11G ... S27 contact forming an additional R_1^1 (7) ring, Fig. 5.

The pairs of molecules generated in this fashion are further

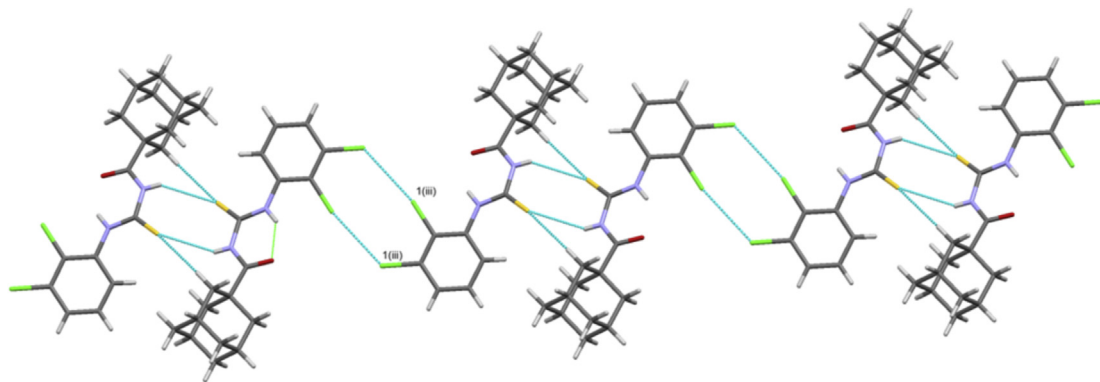


Fig. 2. Sheets of molecules of **1** parallel to (1, -2, 2) with hydrogen bonds drawn, here and in subsequent Figures, as blue dashed lines; 1 (iii) = 3-x, 2-y, 2-z). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

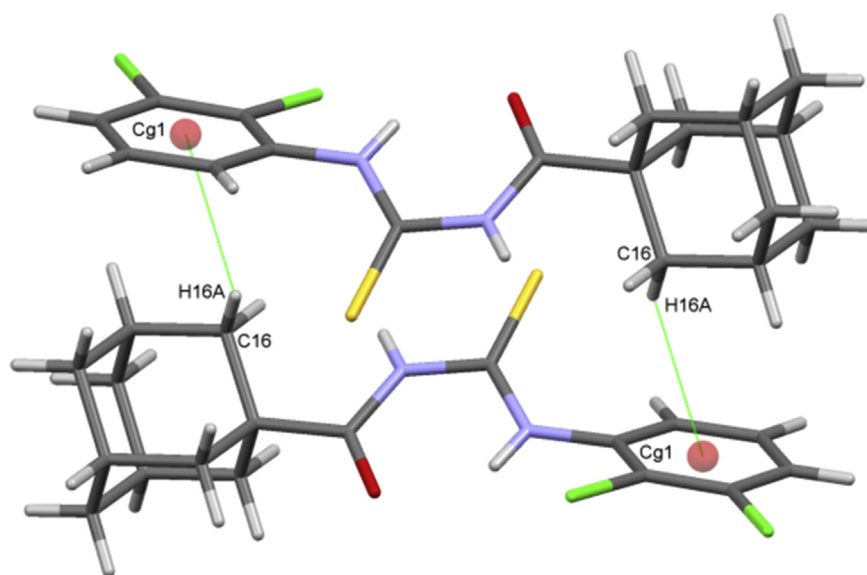


Fig. 3. C–H ... π inversion dimers linking molecules of **1**; C–H ... π contacts are drawn, here and in subsequent Figures, as dotted green lines with ring centroids displayed as coloured spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aggregated by a series of C–H ... π contacts [44] that link **2** (1) and **2** (2) molecules into pairs in a head to head configuration. These pairs are in turn connected head to tail by an additional C–H ... π interaction, to form zig-zag rows along *b*, as shown in Fig. 6 and Table 3. The net effect of this series of contacts is again to stack the molecules along *a*, Fig 7.

3.3. Vibrational properties

The solid phase infrared and Raman spectra for the two species have been measured. The measurement of the Raman spectrum results in a challenging task due to the high fluorescence displayed by both substances. Acceptable spectra were acquired by using the red (647.1 nm) and green (514.5 nm) excitation lines for **1** and **2**, respectively. The vibrational spectra are given in Fig. 8. These results are analyzed in terms of the computed harmonic frequencies calculated for the optimized geometrical structure at the B3LYP/6–311++G (d,p) level. Table S1 (supporting information) collects the vibrational data with tentative mode assignment for the two compounds here studied.

3.3.1. Acyl-thiourea group $-C(O)NHC(S)NH-$ vibrations

Two N–H stretching modes are expected above 3000 cm^{-1} in the vibrational spectra of 1-acyl-3-monosubstituted thioureas. The intramolecular $N2-H\cdots O=C$ hydrogen bond produces a red-shift and band intensification for the corresponding stretching. The infrared spectra of **1** and **2** shown the presence of broad bands with maxima at 3385 (3356 sh) and 3353 (3332 sh) cm^{-1} , which are assigned to the N–H stretching modes. The computed $\nu(N2-H)$ values are 3366 and 3316 cm^{-1} lower than the corresponding $\nu(N1-H)$.

Low values (typically below 1700 cm^{-1}) for the $\nu(C=O)$ stretching mode is characteristic of 1-acyl-3-(mono)substituted thioureas, with a strong intramolecular $N2-H\cdots O=C$ hydrogen bond. Intense infrared absorptions at 1682 and 1681 cm^{-1} (1675 cm^{-1} in Raman) are observed for **1** and **2**, respectively, which are assigned to the $\nu(C=O)$ modes, in excellent agreement with previous studies on 1-(adamantane-1-carbonyl) substituted thioureas [17,18] and with the computed values at 1711 and 1716 cm^{-1} , respectively.

The $\delta(N-H)$ deformation modes of the amide and thioamide groups are expected to appear as two well-resolved and intense absorptions in the $1500\text{--}1600\text{ cm}^{-1}$ range of the IR spectrum [45].

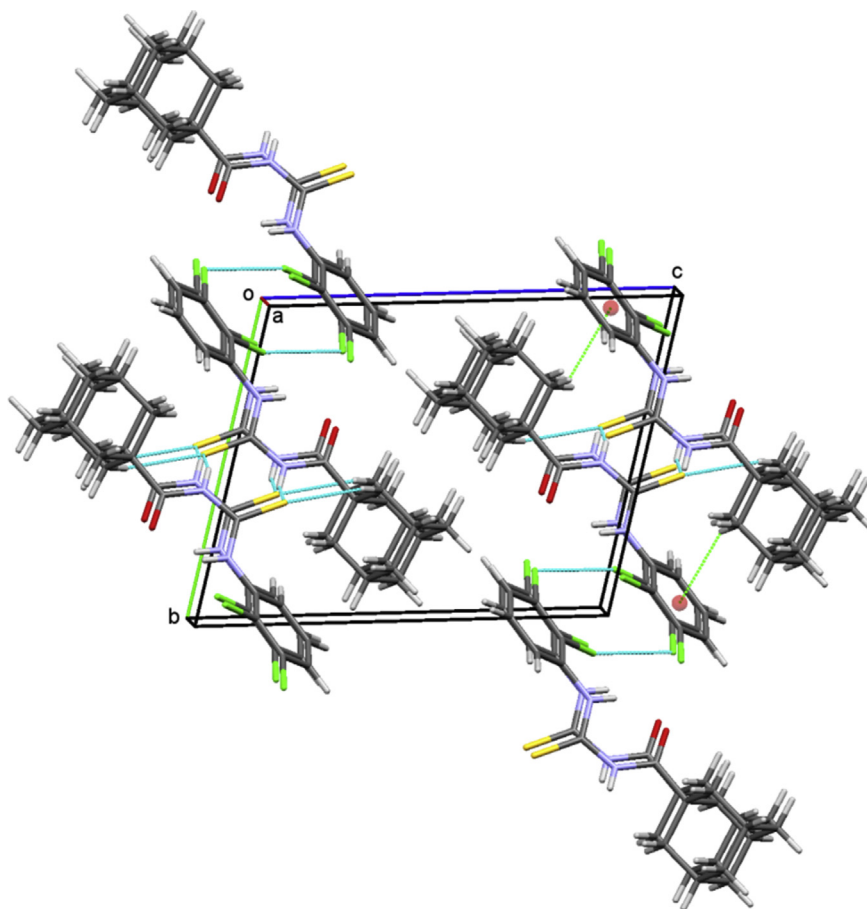


Fig. 4. Overall packing for **1** showing molecules stacked along *a*. Representative C–H ... π contacts are shown as dotted green lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

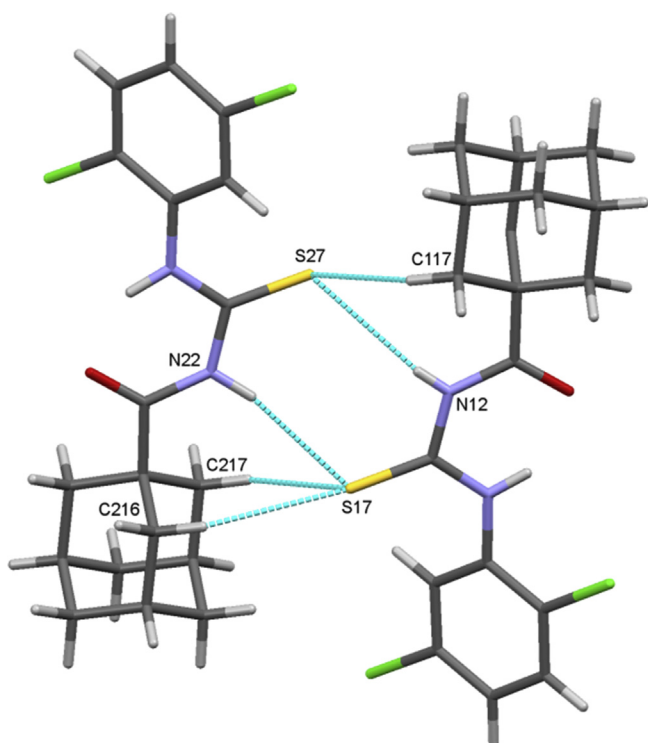


Fig. 5. N–H...S and C–H...S hydrogen bonds linking **2** (1) and **2** (2) molecules.

In the present case, the infrared spectra of compounds **1** and **2** show similar features in this region, with intense bands at 1540 and 1546 cm^{-1} , respectively, which are assigned as $\delta(\text{N1-H})$. The Raman counterparts correspond to medium intense signals at 1541 and 1540 cm^{-1} , respectively. Moreover, the most intense infrared absorptions appear at 1512 and 1516 cm^{-1} for **1** and **2**, respectively, assigned to the $\delta(\text{N1-H})$, in good agreement with the B3LYP/6–311++G (d,p) calculations, with computed values at 1542 and 1544 cm^{-1} with the highest band intensity.

The $\nu(\text{C-N})$ stretching mode (C2–N7 and C12–N17 for **1** and **2**, respectively) is observed at relatively low frequencies, 1160 cm^{-1} (1160 cm^{-1} in Raman) and 1164 cm^{-1} (1173 cm^{-1} Raman) for compound **1** and **2**, respectively, suggesting a little resonance contribution between the amide and thioamide-like groups [46].

The strong intensity IR absorptions observed at 744 cm^{-1} (745 cm^{-1} Raman) for compounds **1** and the strong band in the Raman spectrum of **2** at 740 cm^{-1} are tentatively assigned to the $\nu(\text{C=S})$ mode. This assignment is in agreement with previously studied acyl-thiourea derivatives [17,18], and the low frequency values observed for this vibration (in the thiourea molecule the $\nu(\text{C=S})$ amounts to 1094 cm^{-1} [47]) can be associated with the formation of $\text{C=S}\cdots\text{H-X}$ intermolecular hydrogen bonds.

3.3.2. Adamantane group vibrations

The adamantyl group is responsible for a series of C–H and C–C stretchings located in the 2950–2850 cm^{-1} and 1000–950 cm^{-1} ranges, as well as $>\text{CH}_2$, C–H and CCC deformation and rocking modes appearing in the 1400–1200 cm^{-1} spectral range and below

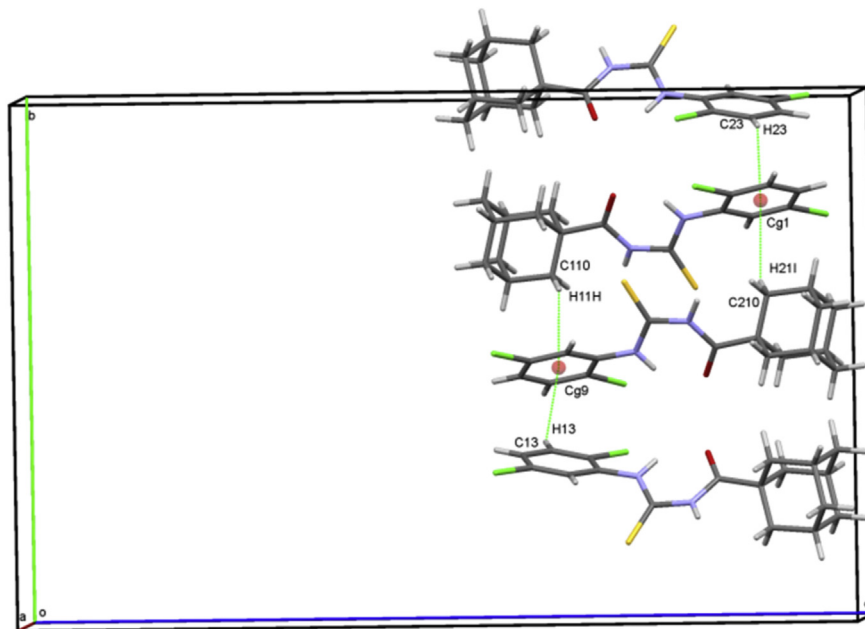


Fig. 6. C–H ... π contacts for **2**.

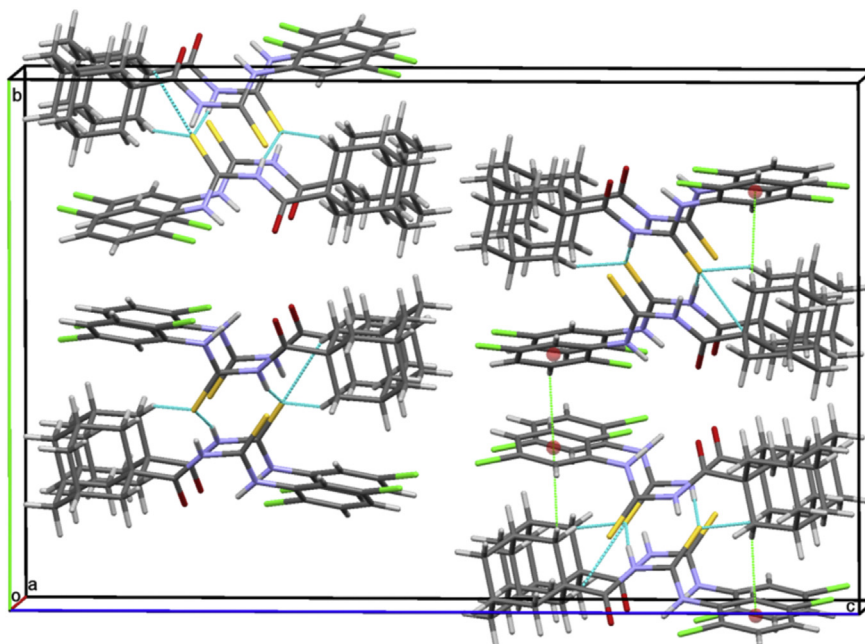


Fig. 7. Overall packing for **2** showing molecules stacked along *a*. Representative C–H ... π contacts are shown as dotted green lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

800 cm^{-1} , respectively. The strong and characteristic band observed in the Raman spectrum at 775 cm^{-1} and 780 cm^{-1} for **1** and **2**, respectively, is assigned with confidence to the “breathing mode”, in agreement with the Raman spectra observed for the parent adamantane molecule [48].

3.3.3. Phenyl group vibrations

The normal modes associated with the $\nu(\text{C–H})$ and $\nu(\text{C}=\text{C})$ stretching vibrations are observed in the typical range with values around 2950 cm^{-1} and below 1600 cm^{-1} , respectively. The C–Cl stretching vibrations are observed as coupled modes at 756 and

754 cm^{-1} in the antisymmetric motion [$\nu_{\text{as}}(\text{C–Cl})$] and the corresponding symmetric mode at 590 and 602 cm^{-1} (611 cm^{-1} in Raman) for compounds **1** and **2**, respectively. These assignments are in good agreement with the vibrational data reported for the related di-chloro substituted benzene species [49].

4. Conclusions

Two novel isomeric 1-(adamantan-1-ylcarbonyl)-3-(di-chlorophenyl) thiourea derivatives were prepared and their structural and spectroscopic properties have been determined. The central

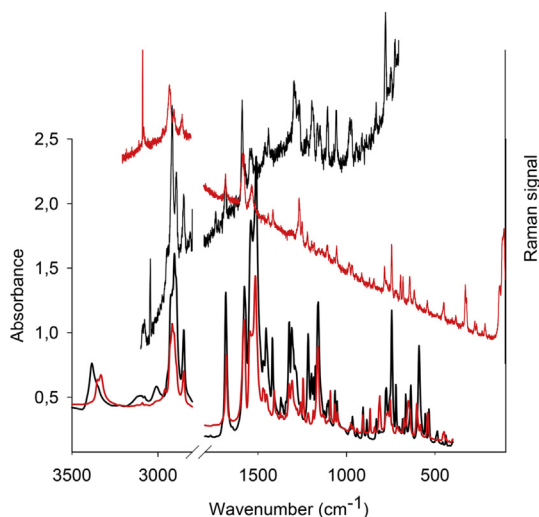


Fig. 8. Infrared and Raman spectra for compounds **1** (black) and **2** (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

–C(O)NHC(S)NH– moiety adopts a nearly planar structure with the C=O and C=S double bond oriented toward opposite directions, a conformation that favors a strong C=O⋯H–N intramolecular hydrogen bond forming S (6) rings. Despite the close similarities between both compounds, isomerism is absent: compound **1** crystallizes in the space group P-1 with $Z = 2$, while compound **2** crystallizes in the orthorhombic system ($P 2_1 2_1 2_1$) with $Z = 8$. Inversion dimers with an R_2^2 (8) ring motif are observed for **1** and **2**, an assemblage that is assisted by strong N–H⋯S=C hydrogen bonds. However, dissimilar π -stacking and Cl⋯Cl intermolecular interactions are observed for the title compounds, clearly influenced by the different di-chlorophenyl substitution at the thiourea core. The experimental infrared and Raman spectra were interpreted with the help of quantum chemical calculations. As expected, the vibrational spectra of both isomers display similar features in the characteristic functional groups regions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.molstruc.2016.09.039>. These data include MOL files and InChIKeys of the most important compounds described in this article.

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