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Synthesis, structural and vibrational properties of 1-(4-Fluorobenzoyl)-3-(isomeric fluorophenyl)thioureas

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1. Introduction

1-Aroyl-3-arylthioureas found a wide diversity of applications in heterocyclic syntheses, metal complexes and molecular electronics and exhibit an array of biological activities [1-4]. Thus, besides the academic interest, N,N-dialkyl-N'-aroyl thioureas are efficient ligands for the separation of platinum group metals [5]. Thiourea complexes are starting materials in chemical spray pyrolysis (CSP) processes which are used to produce thin films of binary and ternary sulfides [6]. Fluorinated aryl thioureas represent a new class of potent anti-trypanosomal agents [7] and also a novel class of potent influenza virus neuraminidase inhibitors [8]. 1,3-Dialkyl or diaryl thioureas exhibit significant antifungal activity against plant pathogens Pyricularia oryzae and Drechslera oryzae [9]. N-Aryl *N*-phenyl thioureas have been developed as anion-binding site in a hydrogen-bonding receptor [10]. Thiacalix [4] arenes containing thioureas are neutral receptors towards α_{α} -dicarboxylate anions [11] and N-4-substituted-benzyl-N'-ter-butylbenzyl thioureas are vanilloid receptors ligands and antagonists in rat DRG neurons [12]. 1-Benzoyl-3-(4,6-disubstituted-pyrimidinyl) thioureas have shown excellent herbicidal activity [13]. Thioureas have also extensively been used in enantioselective synthesis, such as

ABSTRACT

The 1-(4-Fluorobenzoyl)-3-(isomeric fluorophenyl)thioureas (1–3) were prepared by the reaction of 4-fluorobenzoyl isothiocyanate produced *in situ* with isomeric fluoroanilines in dry acetonitrile in good yields. The novel compounds were characterized by multinuclear (¹H and ¹³C) NMR, elemental analyses and FTIR spectroscopy techniques. Structural and conformational properties of compounds 1–3 have been analyzed using a combined approach including X-ray diffraction, vibrational spectra and theoretical calculation methods. The carbonyl and thiourea groups are almost planar and the conformation adopted by the C=S and the C=O double bonds is antiperiplanar, in a conformation which is stabilized by intramolecular N–H···O hydrogen bond. Crystal packing shows molecules connected by intermolecular N–H···S=C hydrogen bonds to form centrosymmetric dimers.

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nitro-Mannich reactions, Aza-Henry reaction, and the Michael Addition [14–16]. In particular, fluorinated thioureas are convenient synthons for preparation of versatile fluorine-containing heterocycles: [1,3]-benzothiazin-4-ones [17], 1-aryl-2-ethylthioquinazolin-4-one, thiazolidine and 1*H*-1,2,4-triazoles [18].

Fabbrizzi et al. reported that substituted-phenyl urea compounds interacts through hydrogen bonding with a variety of oxoanions to give bright colored complexes [19]. A variety of receptors containing the urea and the thiourea groups have been designed for anion recognition [20]. In this context, the molecular structure and conformational flexibility are important properties for determining the donor–acceptor capabilities [21,22]. Also the thioureas can denature proteins, and inhibit the formation of micelles. Therefore the conformational issues in thioureas are comparable to those arising in folded proteins, and a complete understanding of these effects require understanding the effects of intermolecular hydrogen bonding interactions and hydrophobic interactions [20].

In view of the above mentioned facts and in continuation of our work on the synthesis and structural studies of thioureas, here we report the preparation, characterization and structural determination of three novel 1-(4-fluorobenzoyl)-3-(isomeric fluorophenyl)thiourea derivatives (**1–3**). Vibrational and conformational properties are studied by using quantum chemical calculations and vibrational spectroscopy techniques.





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Scheme 1.

2. Results and discussion

2.1. Synthesis and characterization

The title 1-(4-fluorobenzoyl)-3-(isomeric fluorophenyl) thioureas were prepared using a method similar to that reported earlier for related 1-(2-chlorobenzoyl)-3-(isomeric fluorophenyl)thiourea isomers [23] in 60–84% yields (Scheme 1). Table 1 gives the elemental, mass spectrometry and NMR spectroscopic data of compounds (1–3).

2.2. X-ray molecular structure

The molecular structures of compounds **1–3** as determined in the crystalline phase are shown in Figs. 1–3, respectively and Table 2 includes selected geometric parameters derived from the structure refinement, as well as those obtained from quantum chemical calculations.

The three molecular structures differ from the fluorosubstitution pattern of the thiobenzamide ring. Minor differences have been observed in the molecular geometry determined for the three isomers when the crystal structure is compared. For example, the two aromatic planes form dihedral angles each of $38.20(4)^\circ$, $8.20(12)^\circ$ and $43.81(9)^\circ$ for **1–3**, respectively. The carbonyl and thiourea groups O1/C8/N2/C7/S1/N1 are almost planar, largest deviations from mean planes are 0.074(1), 0.053(2), and 0.019(3) Å for **1**, **2**, and **3**, respectively. Associated are intramolecular N1–H···O1 hydrogen bonds forming six-membered rings for all three structures. Dihedral angles between these carbonyl thiourea planes and the fluorophenyl/*p*-fluorophenyl rings measure for **1**: $21.35(5)^\circ/18.51(6)^\circ$, for **2**: $14.44(11)^\circ/22.57(10)^\circ$, for **3**: $52.32(7)^\circ/9.24(13)^\circ$.

It was observed that the amidic N2–C8 [1.377(2) Å] and thioamide N1–C7 [1.401(2) Å] bond lengths (mean values are given) are shorter than C—N single bond [24], indicating a partial double bond character. This observation indicates that resonance interactions are extended over the whole planar —C(O)NHC(S)NH moiety, in accordance with the behavior recently reported for thiocarbamate species [25]. Moreover, it is worth noting that a definite trend in the C—N bond distances has been recognized for these species [5,26], the lengths increasing in the order C7—N1 < C8—N2 < C7—N2. This tendency is also reproduced by the quantum chemical calculations (see Table 1), suggesting that intramolecular electronic effects are responsible for the observed N—C bond lengths values. The different fluoro substitution has no significant effect on N1—C1 or N1—C7 bond length parameters.

Crystal packing shows for **1–3** intermolecular N1—H···S hydrogen bonds, forming centrosymmetric dimers, as shown in Figs. 4–6, with N—H···S contacts of 2.594, 2.908 and 2.781 Å, respectively. This is a well-known crystal motif for *N*-benzoyl-thiourea compounds [25–27], for which the character of the \hat{N} -substituents seems to exert little impact. Intermolecular N1···S short distances amount 3.374(1), 3.722(2) and 3.631(3) Å for compound **1–3**, respectively. The shortest intermolecular C—H···F distances are in the 2.46–2.82 Å range, a short intramolecular N2—H···F distance in **2** measures 2.50 Å.

2.3. Conformational analysis

In principle, the studied compounds may adopt several conformations depending on the relative orientation of the C=O and C=S double bonds and the orientation of substituted phenyl rings. However, several authors [26,27] pointed out that the conformational properties of substituted benzoyl thioureas is mainly dominated by the conformational behavior around the C-N bond joining the amide and thioamide groups. This is also in agreement with our recent work on the conformational space of isomeric 1-(2-chlorobenzoyl)-3-(isomeric fluorophenyl)thiourea derivatives [28]. Based on the X-ray structural results, the substituted phenyl rings were maintained in a conformation close to the experimental X-ray crystal structure, while the potential energy curve around the C7–N2 bond for compounds 1-3 have been theoretically evaluated. Thus, the potential energy curves were computed at the B3LYP level of approximation together with the split-valence triple-zeta basis set 6-311G^{*}, allowing geometry optimizations with the δ (C8N2–C7N1) dihedral angle varying from 0° to 360° in steps of 20°. These curves are displayed in Fig. 7. The three potential energy curves are very similar, showing a clear minimum at δ (C8N2–C7N1) = 0°, corresponding to a local planar structure of the central –C=O–NH–C=S–NH– moiety, with opposite orienta-

Та	ble	1
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Flemental	mass a	nd NMR	spectroscopic	data for	compounds	1_3
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Comp.	Molecular formula (MW)	EIMS (M ⁺ )	Analysi	s (Calcd	./Found)		¹ H NMR	¹³ C NMR
	()		C (%)	H (%)	N (%)	S (%)	$\delta$ (ppm), J (Hz)	$\delta$ (ppm) J (Hz)
1	C ₁₄ H ₁₀ N ₂ OSF ₂ (292.3)	292.0	57.53/ 57.59	3.45/ 3.42	9.58/ 9.62	10.97/ 11.01	12.43 (br s, 1H, NH), 9.65 (br s, 1H, NH), 8.45 (dt, J = 2.1, 7.5 Hz, 1H, Ar—H), 8.07 – 7.05 (m, 7H, Ar—H)	177.5 (C=S), 166.8 (C=O), 164.9 ( $d$ , ¹ $J$ = 250 Hz), 155.0 ( $d$ , ¹ $J$ = 247 Hz,), 133.0 (2C, $d$ , ³ $J$ = 8.25 Hz), 131.6, 127.8 ( $d$ , ³ $J$ = 8.25 Hz), 125.9 ( $d$ , ³ $J$ = 10.5 Hz), 125.2, 124.1 ( $d$ , ⁴ $J$ = 3.75 Hz), 115.6 ( $d$ , ² $J$ = 19.5 Hz), 114.8 (2C, $d$ , ² $J$ = 21.75 Hz)
2	C ₁₄ H ₁₀ N ₂ OSF ₂ (292.3)	292.0	57.53/ 57.47	3.45/ 3.40	9.58/ 9.62	10.97/ 10.93	12.39 (br s, 1H, NH), 9.69 (br s, 1H, NH), 8.08 – 8.00 (2H, m, Ar–H), 7.77 (td, J = 2.1, 10.2 Hz, 1H, Ar–H), 7.43–6.96 (m, 5H, Ar–H)	178.0 (C=S), 166.6 (C=O), 165.5 ( $d$ , ${}^{1}J$ = 244.5 Hz), 164.9 ( $d$ , ${}^{1}J$ = 250 Hz), 138.9 ( $d$ , ${}^{3}J$ = 10.5 Hz), 133.0 (2C, $d$ , ${}^{3}J$ = 8.25 Hz), 131.6, 130.6 ( $d$ , ${}^{3}J$ = 9.75 Hz), 119.4 ( $d$ , ${}^{4}J$ = 3 Hz), 114.8 (2C, $d$ , ${}^{2}J$ = 21.25 Hz), 113.8 ( $d$ , ${}^{2}J$ = 21.75 Hz), 114.8 (2C, $d$ , ${}^{2}J$ = 21.75 Hz)
3	C ₁₄ H ₁₀ N ₂ OSF ₂ (292.3)	292.0	57.53/ 57.59	3.45/ 3.39	9.58/ 9.48	10.97/ 10.90	12.7 (br s, 1H, NH), 9.16 (br s, 1H, NH), 8.07–6.95 (m, 8H, Ar—H).	178.2 (C=S), 166.4 (C=O), 164.9 ( $d$ , $^{1}J$ = 250 Hz), 161.0 ( $d$ , $^{1}J$ = 246 Hz), 133.6 ( $d$ , $^{4}J$ = 3 Hz), 133.0 (2C, $d$ , $^{3}J$ = 8.25 Hz), 131.7, 126.3 (2C, $d$ , $^{3}J$ = 8.25 Hz), 115.8 (2C, $d$ , $^{2}J$ = 22.5 Hz), 114.9 (2C, $d$ , $^{2}J$ = 21.7 Hz)



Fig. 1. Molecular structure of 1. Displacement ellipsoids are shown at the 50% probability level.



Fig. 2. Molecular structure of 2. Displacement ellipsoids are shown at the 50% probability level.



Fig. 3. Molecular structure of 3. Displacement ellipsoids are shown at the 50% probability level.

able 2
xperimental and calculated selected geometric parameters (Å and degrees) for the -NH-C=S-NH-C=O- moiety of compounds 1-3

	1				2			3				
	Exp.	B3LYP/CBSB7	B3LYP/6- 311++G**	B3PW91/6- 311++G**	Exp.	B3LYP/CBSB7	B3LYP/6- 311++G**	B3PW91/6- 311++G**	Exp.	B3LYP/CBSB7	B3LYP/6- 311++G**	B3PW91/6- 311++G**
N1-C7	1.334(2)	1.348	1.349	1.345	1.331(3)	1.347	1.348	1.345	1.328(4)	1.345	1.346	1.342
C=S	1.669(1)	1.671	1.672	1.665	1.666(2)	1.668	1.670	1.664	1.657(3)	1.670	1.672	1.665
C7—N2	1.391(2)	1.409	1.410	1.405	1.405(3)	1.412	1.413	1.408	1.395(4)	1.412	1.414	1.409
N2-C8	1.378(2)	1.382	1.382	1.378	1.382(3)	1.380	1.380	1.375	1.369(4)	1.379	1.380	1.374
C=0	1.227(2)	1.225	1.226	1.225	1.230(2)	1.228	1.229	1.227	1.220(4)	1.228	1.229	1.227
N1-C=S	127.27(9)	129.6	129.6	129.7	127.82(17)	129.8	129.8	129.9	126.0(2)	129.9	129.8	129.9
N1-C7-N2	114.95(10)	114.1	114.1	113.9	114.02(18)	113.7	113.7	113.6	115.3(3)	113.8	113.8	113.6
C7-N2-C8	128.55(10)	130.1	130.3	130.1	128.04(18)	130.1	130.3	130.1	127.4(3)	130.1	130.2	130.1
N2-C=0	122.42(11)	122.6	122.4	122.6	121.8(2)	122.7	122.6	122.7	122.0(3)	122.7	122.6	122.7
C7-N2-C=0	7.5(2)	-3.2	-3.3	-3.4	-4.7(3)	-3.4	-3.6	-3.7	-4.2(5)	-3.5	-3.6	-3.6
N1C7-N2C8	7.55(18)	0.2	0.2	0.2	5.0(3)	0.6	0.7	0.7	4.0(5)	0.6	0.5	0.5



**Fig. 4.** Crystal packing of **1** viewed along [010] with intermolecular  $N-H\cdots S(-x+1, -y+1, -z+1)$  hydrogen bonding pattern indicated as dashed lines. H-atoms not involved in hydrogen bonding are omitted.



**Fig. 5.** Crystal packing of **2** viewed along [010] with intermolecular  $N-H\cdots S(-x+1, -y+1, -z)$  hydrogen bonding pattern indicated as dashed lines. H-atoms not involved in hydrogen bonding are omitted.

tion between the C=O and C=S double bonds. In this conformation the C8=O1 and H-N1 groups form a pseudo six-membered ring, favoring an intramolecular interaction through a hydrogen bond. The computed global minima correspond to the forms present in the crystal of compounds **1–3**. Moreover, the structures with  $\delta$ (C8N2-C7N1) = 180° correspond to a local maxima in the potential energy curve. Two nearly equivalent local minima are observed at  $\delta$ (C8N2-C7N1) values of ca. 150° and 210°. These conformers are located higher in energy by ca. 14–17 kcal mol⁻¹, and correspond to structures with an antiperiplanar orientation between the C8-N2 and C7-N1 bonds.

Additionally, for each molecule here studied, full geometry optimizations and frequency calculations were computed for the more stable conformer with the B3LYP and B3PW91 functionals and the more extended 6-311++G^{**} basis set. Also the B3LYP/CBSB7 level of approximation has been applied. Selected geometrical parameters are given in Table 1. Taking into account the difference in the physical state of the substance, there is a good agreement between



**Fig. 6.** Crystal packing of **3** viewed along [001] with intermolecular  $N-H\cdots S(-x+1, -y+1, z)$  hydrogen bonding pattern indicated as dashed lines. H-atoms not involved in hydrogen bonding are omitted.

the theoretical and the experimental data obtained for the three compounds. The used methods reproduce reasonably well the bond lengths and angles in general, exceptions being found for some values around the sulfur atom, especially when the 6-31G* basis set is used (see Table S1). With moderate large basis sets (6-311++G**), the B3LYP and B3PW91 methods predict the bond length around the thiourea group very well, including the C=S bond. Computed bond angles deviate slightly from the experimental, with maxima deviation found for N1–C=S and C7–N2–C8, which are computed to be higher than the experimental by ca. 2.3 and 1.6 degrees, respectively. The theoretical methods used in the current work compute the orientation of both substituted phenyl groups very similar to that obtained from the X-ray analysis. However, differences were observed for the dihedral angle around the C7-N2 bond, for which the theoretical methods predict a nearly planar structure and N1C7-N2C8 dihedral angles of 7.5(2)°, 5.0(3)° and 4.0(5)° were determined from the X-ray analysis (see Table 1).



**Fig. 7.** Calculated (B3LYP/6-311G*) potential function for internal rotation around the  $\delta$ (C8N2–C7N1) dihedral angle of compounds **1** (–**●**–), **2** (–**■**–) and **3** (–**▲**–). For atom numbering see Figs. 1–3.

#### 2.4. Vibrational analysis

In (thio)amide compounds several infrared absorption bands which are called "(thio)amide bands" are important for studying structural and electronic properties because they are sensitive to intermolecular hydrogen bonding and conformational changes [29,30]. The thioamide bands I, II, III and IV have a large contribution from  $\delta$ (N–H) (I), v(C–N) (II and III) and v(C=S) (IV) motions and are usually reported around 1500, 1300, 1100 and 750  $cm^{-1}$ , respectively [31,32]. For the title species, these bands emerge in a region which is plenty of absorptions from substituent groups, making difficult their identification. The joint analysis of both IR and Raman spectra arises necessary for an unambiguous identification [30]. Moreover, an assignment of the observed vibrational spectra can be assisted by a systematic comparison with the theoretically calculated one. Quantum chemical calculations have been applied [26] and recently density functional theory (DFT) methods were used to predict the vibrational frequencies of related species [28,33,34]. The combination of the B3LYP functional in connection with the CBSB7 basis set was recommended for studying spectroscopic properties of sulfur-containing compounds [35,36]. Thus, experimental and calculated (B3LYP/CBSB7) armonic frequencies (without factor scale) as well as the computed infrared and Raman intensities are given in Table 3. A tentative assignment of the observed bands was carried out by comparison with spectra of related molecules [33,37-41]. Furthermore, simulated infrared and Raman activity spectra obtained with the B3LYP/CBSB7 approximation, together with the experimental spectra are in Figs. S1-3 in the Supporting Information.

The strong IR absorptions at 1670, 1671 and 1667 cm⁻¹ for compounds **1–3**, respectively, were assigned to the v(C=O) modes. Very strong counterparts are observed in the Raman spectra at 1669 cm⁻¹ for the three studied compounds. Calculated frequencies for this mode are also very similar for the three isomers [1731 (**1**), 1725 (**2**) and 1724 (**3**) cm⁻¹] and it is appreciably coupled with the C–N stretch and with the N–H bend, as observed for related compounds [42,43]. Thus, it is quite likely that large anarmonicity effects could account for the difference between the computed and the experimental values for this mode.

Very strong IR absorptions with defined maxima at 1566 (**1**), 1564 (**2**) and 1537 (**3**) cm⁻¹ can be assigned with confidence to the  $\delta$ (N1–H) bending mode in the thioamide group (thioamide

band I), while strong bands located at 1532 (**1**, **2**) and 1537 (**3**) cm⁻¹, are assigned to the same mode in the amide-like N2–H group [ $\delta$ (N2–H)]. Taking compound **1** as illustration, B3YLP/CBSB7 computations predict strong bands due to the  $\delta$ (N1–H) and  $\delta$ (N2–H) normal modes at 1604 and 1556 cm⁻¹, respectively.

Taking into account the vibrational properties reported for the simple thiourea molecule [44], it is expected that the C–N stretching modes, which are usually coupled in symmetric and antisymmetric motions, appear in the 1400–1300 cm⁻¹ region [42]. The situation becomes more complicated if, as for compounds **1–3**, there are inequivalent C–N bonds. Thus, the NCN antisymmetric stretching mode of the thiourea moiety (thioamide band II) is assigned to the intense bands centered at 1346, 1350 and 1346 cm⁻¹ in the infrared spectra of compounds **1–3**, respectively. Computed values at the B3LYP/6-311 + G* level of approximation are 1384, 1386 and 1389 cm⁻¹, respectively, slightly higher than the experimentally observed ones. The symmetric  $v_s$ (NCN) stretching mode (thioamide band III) is tentatively assigned to the band observed at 1145, 1146 and 1152 cm⁻¹, for compound **1–3**, respectively.

Weak IR absorptions observed around 750 cm⁻¹ with medium intensity Raman signals were assigned to the v(C=S) mode for compounds **1–3**, in good agreement with the calculated values (Table 2) and with assignments proposed for similar species [34,45]. This mode is usually associated with the thioamide band IV. However, quantum chemical calculations also predict a high contribution of this motion to a second mode, higher in frequency and associated also with the  $v_s(CNC)$  normal mode. It should be noted that in the thiourea molecule, the v(C=S) is assigned to the absorption appeared at 1094 cm⁻¹ in the infrared spectrum (1105 cm⁻¹ Raman) [44], while higher values – up to 1325 cm⁻¹ – have been also reported [40]. The formation of C=S···H–X intermolecular hydrogen bonds seems to strongly affect the frequency of the v(C=S) mode [37], as determined from the X-ray analysis in the title species.

With the aim to determine, at least approximately, the effect of hydrogen bonding on the molecular structure and vibrational properties, we performed theoretical calculations (B3LYP/6-31G^{*}) for an arrangement of two molecules in an attempt to simulate the crystal packing. The optimized geometries for the  $C_i$  dimmers of **1–3** are given in Fig. S1 and relevant computed geometrical parameters are listed in Table S1 in the Supporting Material. The geometrical structure computed for the dimmers and monomers are very similar, with expected variation in the C=S bond distances, which are ca. 0.01 Å longer and the S=C-N1 bond angles, which are ca. 2° lower in the dimmers for the three compounds here studied.

The dimmers formation influences the harmonic vibrational spectra mainly by changing the relative intensity of the normal modes related with the N–H group. Thus, an strong increment in the intensity of both v(N2–H) and  $\delta(N2–H)$  fundamentals with respect to the monomers are computed, in perfect agreement with the experimental spectra.

# 3. Conclusions

Conformational and structural properties of three novel 1-(4-fluorobenzoyl)-3-(isomeric fluorophenyl)thiourea derivatives (1-3) were determined by using infrared spectroscopy and X-ray diffraction analysis. The central -C=O-NH-C=S-NH- moiety adopts a planar structure with a preferred antiperiplanar orientation of both C=O and C=S double bonds. In this conformation a strong intramolecular hydrogen bond between the C=O and H-N1 groups is formed, favored by a pseudo six-membered ring involving the thiourea skeleton. This form is present in the crystal

# Table 3

Experimental and theoretical vibrational data (cm⁻¹) for isomers **1–3**.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	FTIR ^a	IR ^a					Calculated ^b			Proposed assignment
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	2	3	1	2	3	1	2	3	approximate description ^c
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3267 m	3327 m	3362 m				3618(37.5, 0.02)	3618 (37.6, 0.02)	3618 (37.6, 0.02)	v(N2—H)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	3196 sh		3230 m, br				3318 (372.1, 0.09)	3339 (376.1, 0.07)	3336 (367.6, 0.08)	v(N1—H)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3119 vw			3080 m	3077 m	3083 m	3241 (10.6, 0.02)	3242 (19.6, 0.01)	3239 (10.7, 0.02)	v(C—H)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	3049 w		3044 m	3062 w	3048 w, sh		3212 (2.8, 0.05)	3213 (2.6, 0.04)	3212 (2.6, 0.05)	v(C-H)
2928 sh2928 vw $3205 (5.8, 0.09)$ $3207 (1.1, 0.04)$ $3204 (3.0, 0.04)$ $v(C-H)$ 2852 vw2845 vw $3199 (0.8, 0.03)$ $3199 (0.9, 0.04)$ $3200 (4.1, 0.02)$ $v(C-H)$ 1670 s1671 s1667 s1669 s1669 vs1669 s1731 (123.7, 0.2)1725 (106.5, 0.21)1724 (122.9, 0.15) $v(C-O)$ 1617 s1605 s1616 vs1611 vs1604 vs1659 (162.7, 1)1660 (124.1, 1)1659 (249.3, 1) $v(C-C)$ 1598 s1605 s1601 s1593 w, sh1644 (384.8, 0.39)1646 (309.5, 0.1)1646 (224.8, 0.09) $v(C-C)$ 1566 vs1564 vs1571 s1555 s1564 vs1564 s1604 (390.5, 0.57)1612 (599.1, 0.80)1614 (334.1, 0.89) $\delta(N2-H)$ 1532 vs1537 vs1514 w1554 s1556 (255.2, 0.08)1555 (270.6, 0.08)1556 (308.2, 0.08) $\delta(N2-H)$ 1502 s1500s1506 vs1506 vs1506 vs1548 s1489 w1485 w1493 m1518 (274.6, 0.15)1516 (130.2, 0.07)1534 (378.7, 1.21) $v(C-C)$ 1460 sh1452 sh1408 w1413 vw1410 w1440 (21.9, 0.06)1441 (28.4, 0.07)1440 (22.6, 0.06) $v(C-C)$ 1366 vs1350 vs1346 m1344 m1352 m1357 w hr1384 (645 4, 0.68)1386 (577 5, 0.63)1389 (606 4, 0.15) $v_c$ (NCN)	3014 m	2980 m					3206 (1.1, 0.04)	3208 (3.2, 0.08)	3207 (1.1, 0.06)	v(C-H)
2852 vw2845 vw2845 vw $3199(0.8, 0.03)$ $3199(0.9, 0.04)$ $3200(4.1, 0.02)$ $v(C-H)$ 1670 s1671 s1667 s1669 s1669 vs1669 s1731(123.7, 0.2)1725(106.5, 0.21)1724(122.9, 0.15) $v(C=O)$ 1617 s1608 s1616 vs1611 vs1604 vs1659(162.7, 1)1660(124.1, 1)1559(249.3, 1) $v(C=C)$ 1598 s1605 s1601 s1593 w, sh1644(384.8, 0.39)1646(309.5, 0.1)1646(224.8, 0.09) $v(C=C)$ 1566 vs1564 vs1571 s1555 s1564 vs1564 s1604(390.5, 0.57)1612(599.1, 0.80)1614(334.1, 0.89) $\delta(N1-H)$ 1532 vs1532 vs1537 vs1514 w1554 s1556(252.2, 0.08)1555 (270.6, 0.08)1556(308.2, 0.08) $\delta(N2-H)$ 1502 s1500s1506 vs1506 vs1506 vs1489 w1485 w1493 m1518(274.6, 0.15)1516 (130.2, 0.07)1534(378.7, 1.21) $v(C-C)$ 1460 sh1452 sh1408 w1413 vw1410 w1440(21.9, 0.06)1441(28.4, 0.07)1440(22.6, 0.06) $v(C-C)$ 1366 vs1350 vs1346 m1344 m1352 m1357 w hr1384(6454, 0.68)1386(577.5, 0.63)1389(606.4, 0.15) $v_c(NCN)$	2928 sh	2928 vw					3205 (5.8, 0.09)	3207 (1.1, 0.04)	3204 (3.0, 0.04)	v(C—H)
1670 s1671 s1667 s1669 s1669 vs1669 s1731 (123.7, 0.2)1725 (106.5, 0.21)1724 (122.9, 0.15) $v(C=0)$ 1617 s1608 s1616 vs1611 vs1604 vs1659 (162.7, 1)1660 (124.1, 1)1659 (249.3, 1) $v(C=C)$ 1598 s1605 s1601 s1593 w, sh1644 (384.8, 0.39)1646 (309.5, 0.1)1646 (224.8, 0.09) $v(C=C)$ 1566 vs1564 vs1571 s1555 s1564 vs1564 s1604 (390.5, 0.57)1612 (599.1, 0.80)1614 (334.1, 0.89) $\delta(N1=H)$ 1532 vs1532 vs1537 vs1514 w1554 s1556 (255.2, 0.08)1555 (270.6, 0.08)1556 (308.2, 0.08) $\delta(N2=H)$ 1502 s1500s1506 vs1506 vs1508 vs1489 w1485 w1493 m1518 (274.6, 0.15)1516 (130.2, 0.07)1534 (378.7, 1.21) $v(C=C)$ 1485 vs1484 s1489 w1413 vw1410 w1440 (21.9, 0.06)1441 (28.4, 0.07)1440 (22.6, 0.06) $v(C=C)$ 1409 m1412 m1408 m1408 w1413 vw1410 w1440 (21.9, 0.06)1441 (28.4, 0.07)1440 (22.6, 0.06) $v(C=C)$ 1366 vs1350 vs1346 m1344 m1352 m1357 w br1384 (645 4, 0.68)1386 (577 5, 0.63)1389 (606 4, 0.15) $v_v(NCN)$	2852 vw	2845 vw					3199 (0.8, 0.03)	3199 (0.9, 0.04)	3200 (4.1, 0.02)	v(C-H)
1617 s1608 s1616 vs1611 vs1604 vs1659 (162,7,1)1660 (124,1,1)1659 (249,3,1) $v(C-C)$ 1598 s1605 s1601 s1593 w, sh1644 (384.8, 0.39)1646 (309.5, 0.1)1646 (224.8, 0.09) $v(C-C)$ 1566 vs1564 vs1571 s1555 s1564 vs1564 s1604 (390.5, 0.57)1612 (599.1, 0.80)1614 (334.1, 0.89) $\delta(N1-H)$ 1532 vs1532 vs1537 vs1514 w1554 s1556 (255.2, 0.08)1555 (270.6, 0.08)1556 (308.2, 0.08) $\delta(N2-H)$ 1502 s1500s1506 vs1509 m1536 (134.1, 0.17)1535 (240.7, 0.08)1542 (198.1, 0.20) $v(C-C)$ 1485 vs1484 s1489 w1485 w1493 m1518 (274.6, 0.15)1516 (130.2, 0.07)1534 (378.7, 1.21) $v(C-C)$ 1460 sh1452 sh1410 w1410 w1440 (21.9, 0.06)1441 (28.4, 0.07)1440 (22.6, 0.06) $v(C-C)$ 1366 vs1380 (577 5, 0.63)1389 (606 4, 0.15) $v_{v}$ (NCN)	1670 s	1671 s	1667 s	1669 s	1669 vs	1669 s	1731 (123.7. 0.2)	1725 (106.5, 0.21)	1724 (122.9, 0.15)	v(C=0)
1598 s1605 s1601 s1593 w, sh1644 (384,8, 0.39)1646 (309.5, 0.1)1646 (224,8, 0.09) $v(C-C)$ 1566 vs1564 vs1571 s1555 s1564 vs1564 s1604 (390.5, 0.57)1612 (599.1, 0.80)1614 (334.1, 0.89) $\delta(N1-H)$ 1532 vs1532 vs1537 vs1514 w1554 s1556 (255.2, 0.08)1555 (270.6, 0.08)1556 (308.2, 0.08) $\delta(N2-H)$ 1502 s1500s1506 vs1509m1536 (134.1, 0.17)1535 (240.7, 0.08)1542 (198.1, 0.20) $v(C-C)$ 1485 vs1484 s1489 w1485 w1493 m1518 (274.6, 0.15)1516 (130.2, 0.07)1534 (378.7, 1.21) $v(C-C)$ 1460 sh1452 sh1410 w1410 w1440 (21.9, 0.06)1441 (28.4, 0.07)1440 (22.6, 0.06) $v(C-C)$ 1366 vs1346 m1344 m1352 m1357 w br1384 (645 4, 0.68)1386 (577 5, 0.63)1389 (606 4, 0.15) $v_c(NCN)$	1617 s	1608 s		1616 vs	1611 vs	1604 vs	1659 (162.7, 1)	1660 (124.1, 1)	1659 (249.3, 1)	$v(\mathbf{C}-\mathbf{C})$
1566 vs       1564 vs       1571 s       1555 s       1564 vs       1564 s       1604 (390.5, 0.57)       1612 (599.1, 0.80)       1614 (334.1, 0.89) $\delta$ (N1-H)         1532 vs       1537 vs       1514 w       1554 s       1566 (255.2, 0.08)       1555 (270.6, 0.08)       1556 (308.2, 0.08) $\delta$ (N2-H)         1502 s       1500s       1506 vs       1509m       1536 (134.1, 0.17)       1535 (240.7, 0.08)       1542 (198.1, 0.20)       v(C-C)         1485 vs       1484 s       1489 w       1485 w       1493 m       1518 (274.6, 0.15)       1516 (130.2, 0.07)       1534 (378.7, 1.21)       v(C-C)         1460 sh       1452 sh       1410 w       1410 w       1440 (21.9, 0.06)       1441 (28.4, 0.07)       1440 (22.6, 0.06)       v(C-C)         1366 vs       1350 vs       1346 m       1344 m       1352 m       1357 w br       1384 (645 4, 0.68)       1386 (577 5, 0.63)       1389 (606 4, 0.15)       v. (NCN)	1598 s		1605 s	1601 s	1593 w sh		1644 (384 8, 0.39)	1646(3095,01)	1646 (224 8 0.09)	$v(\mathbf{C}-\mathbf{C})$
1532 vs       1537 vs       1514 w       1554 s       1556 (252, 0.08)       1555 (270, 6, 0.08)       1556 (382, 0.08) $\delta(N2-H)$ 1502 s       1500 s       1500 vs       1500 m       1556 (252, 0.08)       1555 (270, 6, 0.08)       1556 (382, 0.08) $\delta(N2-H)$ 1502 s       1500 s       1500 vs       1500 m       1556 (252, 0.08)       1555 (270, 6, 0.08)       1556 (382, 0.08) $\delta(N2-H)$ 1485 vs       1484 s       1489 w       1485 w       1493 m       1518 (274, 6, 0.15)       1516 (130, 2, 0.07)       1534 (378, 7, 1.21)       v(C-C)         1460 sh       1452 sh       1410 w       1410 w       1440 (21, 9, 0.06)       1441 (28, 4, 0.07)       1440 (22, 6, 0.06)       v(C-C)         1366 vs       1350 vs       1346 m       1344 m       1352 m       1357 w br       1384 (645 4, 0.68)       1386 (577 5, 0.63)       1389 (606 4, 0.15)       v. (NCN)	1566 vs	1564 vs	1571 s	1555 s	1564 vs	1564 s	1604 (390 5, 0.57)	1612 (599.1, 0.80)	1614 (334 1 0.89)	$\delta(N1-H)$
1502 s       1506 vs       1506 vs       1509 m       1536 (134.1, 0.17)       1535 (240.7, 0.08)       1542 (198.1, 0.20)       v(C-C)         1485 vs       1484 s       1489 w       1485 w       1493 m       1518 (274.6, 0.15)       1516 (130.2, 0.07)       1534 (378.7, 1.21)       v(C-C)         1460 sh       1452 sh       1410 w       1440 (21.9, 0.06)       1441 (28.4, 0.07)       1440 (22.6, 0.06)       v(C-C)         1346 vs       1350 vs       1346 m       1342 m       1357 m br       1384 (645 4, 0.68)       1386 (577 5, 0.63)       1389 (606 4, 0.15)       v. (NCN)	1532 vs	1532 vs	1537 vs	1514 w	100110	1554 s	1556 (255.2, 0.08)	1555 (270.6, 0.08)	1556 (308.2, 0.08)	$\delta(N2-H)$
1485 vs       1484 s       1489 w       1485 w       1493 m       1518 (274.6, 0.15)       1516 (130.2, 0.07)       1512 (130.1, 0.20)       v(C-C)         1460 sh       1452 sh         1409 m       1412 m       1408 m       1413 vw       1410 w       1440 (21.9, 0.06)       1441 (28.4, 0.07)       1440 (22.6, 0.06)       v(C-C)         1366 vs       1350 vs       1346 m       1342 m       1357 w br       1384 (6454 0.68)       1386 (577 5.0.63)       1389 (6064 0.15)       v. (NCN)	1502 s	1500s	1506 vs	10111		1509m	1536 (134.1, 0.17)	1535 (240.7, 0.08)	1542 (198 1 0 20)	$v(\mathbf{C}-\mathbf{C})$
1460 sh       1452 sh         1409 m       1412 m         1460 sh       1410 w         1409 m       1412 m         1360 vs       1346 m         1360 vs       1346 m         1360 vs       1346 m         1400 vs       1357 vs         1400 vs       1440 (21.9, 0.06)         1410 vs       1440 (21.9, 0.06)         1440 (22.6, 0.06)       v(C-C)         1360 vs       1350 vs         1346 m       1352 m         1357 vs       1384 (6454 0.68)       1386 (577 5 0.63)       1389 (6064 0.15)         vs       1350 vs       1346 m       1357 m       1357 vs       1384 (6454 0.68)       1386 (577 5 0.63)       1389 (6064 0.15)	1485 vs	1484 s	1500 15	1489 w	1485 w	1493 m	1518 (274.6, 0.15)	1516 (130.2, 0.07)	1534 (378 7 1 21)	$v(\mathbf{C} - \mathbf{C})$
1400 sn 1412 m 1408 m 1408 w 1413 vw 1410 w 1440 (21.9, 0.06) 1441 (28.4, 0.07) 1440 (22.6, 0.06) v(C-C) 1346 vs 1350 vs 1346 m 1344 m 1352 m 1357 w br 1384 (6454, 0.68) 1386 (5775, 0.63) 1389 (6064, 0.15) v. (NCN)	1460 sh	1452 sh		1105 W	1105 W	1155 111	1510 (27 1.0; 0.15)	1510 (150.2, 0.07)	1551 (576.7, 1.21)	
1360 vs $1350$ vs $1346$ m $1344$ m $1352$ m $1357$ w br $1384(6424.068)$ $1386(5775.063)$ $1389(6064.015)$ v. (NCN)	1400 m	1412 m	1/08 m	1/08 w	1/13 1/14	1/10 w	1440 (21.9, 0.06)	1441 (28 4 0 07)	1440 (22.6, 0.06)	$v(\mathbf{C}-\mathbf{C})$
	1346 vs	1350 vs	1346 m	1344 m	1352 m	1357 w br	1384 (645 4 0.68)	1386 (577 5 0.63)	1389(6064, 0.15)	v (NCN)
$\frac{1216}{1216} m = \frac{1212}{1216} m = \frac{1216}{1216} m = \frac{1216}{1216} m = \frac{1216}{1216} (100, 50.17) = \frac{1206}{1256} (100, 70.12) = \frac{1216}{1256} (100, 70.12) = $	1340 VS 1216 m	1212 c	1219 w	1215 m	1332 III 1210 w	1214 m	1384 (045.4, 0.08)	1380(377.3, 0.03) 1254(1027, 0.12)	1246 (48 2 0 25)	$V_{as}(\mathbf{NCN})$
$1310 \text{ m} \qquad 1312 \text{ s} \qquad 1316 \text{ w} \qquad 1313 \text{ m} \qquad 1316 \text{ w} \qquad 1314 \text{ m} \qquad 1349 (100.5, 0.17) \qquad 1344 (122.5, 0.12) \qquad 1340 (162.5, 0.23) \qquad y(C-C)$	1295 104	1312 S	1318 W	1212 fl	1310 W	1314 III 1202 w	1349(100.3, 0.17) 1240(128, 0.02)	1334(152.7, 0.12) 1241(72, 0.01)	1340(46.2, 0.23) 1240(162, 0.02)	v(C=C)
$\frac{1265 \text{ vi}}{1265 \text{ c}} = \frac{1267 \text{ m}}{1267 \text{ m}} = \frac{1255 \text{ sii}}{1276 \text{ m}} = \frac{1250 \text{ vi}}{1260 \text{ m}} = \frac{1340 (125, 0.05)}{1290 (505, 0.05)} = \frac{1341 (72, 0.01)}{1291 (72, 0.01)} = \frac{1340 (102, 0.02)}{1290 (505, 0.05)} = \frac{1340 (102, 0.02)}{1290 (102, 0.02)} = \frac{1340 (102, 0.02)}{1200 (102, 0.02)} = 1340 (10$	1263 VW	1278 11	1267 m	1255 SII 1262 m	1278 111	1295 W	1340 (13.8, 0.03)	1341(7.2, 0.01) 1280(122.2, 0.14)	1340(10.2, 0.02) 1270(2165, 0.12)	v(C = V)
$\frac{1202}{1202} = \frac{1203}{1203} = \frac{1203}{120} = \frac{1203}{110} = \frac{1203}{1200} = \frac{1200}{110} = \frac{1200}{1200} = \frac{1200}{1000} =$	1202 S	1205 5	1207 111	1205 11	1251 m	1209 111	1260(30.3, 0.10) 1268(122.2, 0.70)	1269 (133.3, 0.14)	1279(210.3, 0.12) 1260(1510, 0.02)	v(Co-IV2)
$\frac{1245 \text{ sl}_{1111}}{1245 \text{ s}_{1245 \text$	1245 511,111	1245 \$	1004 -	1240 5	1251 111	1220	1268 (122.2, 0.79)	1269 (144.2, 0.06)	1269 (151.9, 0.02)	V(C-F)
$\frac{1237}{123} \times \frac{1234}{123} \times \frac{1239}{123} \times \frac{1239}{123} \times \frac{1239}{123} \times \frac{1232}{123} \times \frac{1232}{123} \times \frac{1230}{123} \times 12$	1237 5		1234 S	1207		1239 VS	1253 (106.8, 0.04)	1260 (25.0, 0.60)	1257 (70.9, 0.80)	V(C8-C9)
$\frac{12201 \text{ vs}}{1222 \text{ (123.6, 0.04)}} = \frac{1219 \text{ m, sn}}{1242 \text{ (43.6, 0.65)}} = \frac{1207 \text{ vw}}{1242 \text{ (43.6, 0.65)}} = \frac{1212 \text{ m, sn}}{1242 \text{ (43.6, 0.65)}} = \frac{1242 \text{ (43.6, 0.65)}}{1242 \text{ (43.6, 0.65)}} = \frac{1242 \text{ (43.6, 0.65)}}{1$	1201 VS	1101 -	1219 m, sn	1207 VW	1120	1157	1222 (123.6, 0.04)	1197 (0.6, 0.06)	1242 (45.6, 0.65)	δ(CΗ)
$\frac{1160 \text{ s}}{1161 \text{ s}} = \frac{1160 \text{ s}}{1160 \text{ s}} = \frac{1158 \text{ m}}{1138 \text{ m}} = \frac{1157 \text{ m}}{1157 \text{ m}} = \frac{1181 (113.5, 0.07)}{1181 (113.5, 0.07)} = \frac{1181 (94.9, 0.22)}{1181 (94.9, 0.22)} = \delta(C-H)$	1160 s	1161 S	1160 s	1158 m	1138 m	1157 m	1181 (113.5, 0.07)	11/1 (29.7, 0.14)	1181 (94.9, 0.22)	$\partial(C - H)$
$1145$ s $1165$ s $1152$ s, sn $1143$ w $1143$ m $1163(203.8, 0.22)$ $1161(265.8, 0.45)$ $1161(252.8, 0.15)$ $v_{s}(NCN)$	1145 s	1146 s	1152 s, sh	1143 w		1143 m	1163 (203.8, 0.22)	1161 (266.8, 0.45)	1161 (252.8, 0.15)	$v_{\rm s}(\rm NCN)$
$\frac{1111}{111} \text{ m} \qquad 1111 \text{ w} \qquad 11126 (46.3, 0.01) \qquad 1125 (55.2, 0.03) \qquad 1128 (18.5, 0.002) \qquad y_{as}(\text{CNC})$	1111 m	1111 w	1111 W	1000	1005	1077	1126 (46.3, 0.01)	1125 (56.2, 0.03)	1128 (18.5, 0.002)	$v_{as}(CNC)$
$1094 \text{ w}$ 1100 w 1098 w 1096 w 1085 w 107/m 1116 (8.6, 0.05) 1103 (3.9, 0.06) 1124 (42.5, 0.14) $\delta(H)$	1094 w	1100 w	1098 w	1096 w	1085 W	1077 m	1116 (8.6, 0.05)	1103 (3.9, 0.06)	1124 (42.5, 0.14)	$\partial(C-H)$
$\frac{1079 \text{ w}}{1072 \text{ w}} = \frac{1075 \text{ w}}{1075 \text{ w}} = \frac{1087 (18.8, 0.12)}{1085 (23.8, 0.12)} = \frac{1085 (23.6, 0.002)}{1085 (23.6, 0.002)} = 1085 (23$	1079 w	1072 vw		1075 W			1087 (18.8, 0.12)	1086 (23.8, 0.12)	1085 (29.6, 0.002)	$v(C=S)/v_s(CNC)$
$1031 \text{ w}  1032 \text{ m}  1002 \text{ vs}  1057 (11.2, 0.14)  1029 (7.1, 0.29)  1029 (6.7, 0.001)  \delta(\text{CCC})$	1031 w			1032 m	1002 vs		1057 (11.2, 0.14)	1029 (7.1, 0.29)	1029 (6.7, 0.001)	$\delta(CCC)$
$1011 \text{ w}  1014 \text{ vw}  1014 \text{ w}  1014 \text{ w}  1029 (8.2, 0.00)  1018 (10.1, 0.001)  1028 (4.3, 0.003)  \delta(\text{CCC})$	1011 w	1014 vw	1014 w				1029 (8.2, 0.00)	1018 (10.1, 0.001)	1028 (4.3, 0.003)	$\delta(CCC)$
960 vw 952 w 946 m 969 (6.1, 0.03) 970 (0.1, 0.002) 969 (7.5, 0.23) δ(N-C7-N)	960 vw			952 w		946 m	969 (6.1, 0.03)	970 (0.1, 0.002)	969 (7.5, 0.23)	$\delta(N-C7-N)$
939 w 956 (0.6, 0.003) 957 (0.9, 0.003) 957 (1.1, 0.001) $\delta$ (C-H)	939 w						956 (0.6, 0.003)	957 (0.9, 0.003)	957 (1.1, 0.001)	$\delta(C-H)$
907 m 900 vw 903 w 952 (5.1, 0.001) 922 (49.9, 0.05) 942 (1.0, 0.002) $\delta$ (C-H)		907 m	900 vw		903 w		952 (5.1, 0.001)	922 (49.9, 0.05)	942 (1.0, 0.002)	$\delta(C-H)$
$862 \text{ w} \qquad 866 \text{ m} \qquad 863 \text{ vw} \qquad 862 \text{ w} \qquad 846 \text{ w} \qquad 866 \text{ vs} \qquad 876 (16.0, 0.06) \qquad 891 (24.0, 0.004) \qquad 878 (9.9, 0.19) \qquad \delta(\text{NC=0})$	862 w	866 m	863 vw	862 w	846 w	866 vs	876 (16.0, 0.06)	891 (24.0, 0.004)	878 (9.9, 0.19)	$\delta(NC=0)$
849 s         852 s         848 m         871 (0.7, 0.004)         887 (8.7, 0.0001)         866 (25.9, 0.002)         δ(C-H)	849 s	852 s	848 m				871 (0.7, 0.004)	887 (8.7, 0.0001)	866 (25.9, 0.002)	$\delta(C-H)$
816 m811 m835 m, sh817 w866 (25.8, 0.005)866 (30.3, 0.007)857 (103.5, 0.003) $\delta$ (C-H)	816 m	811m	835 m, sh	817 w			866 (25.8, 0.005)	866 (30.3, 0.007)	857 (103.5, 0.003)	$\delta(C-H)$
826 m 852 (88.7, 0.003) 853 (3.1, 0.008) 841 (30.6, 0.001) $\rho$ (N1-H)			826 m				852 (88.7, 0.003)	853 (3.1, 0.008)	841 (30.6, 0.001)	$\rho(N1-H)$
799 s         795 m         794 vw         799 w         795 w         794 s         815 (19.9, 0.002)         809 (22.0, 0.08)         812 (7.3, 0.16)         δ(C-N1-C)	799 s	795 m	794 vw	799 w	795 w	794 s	815 (19.9, 0.002)	809 (22.0, 0.08)	812 (7.3, 0.16)	$\delta(C-N1-C)$
764 s 775 w 770 w 768 (49.2, 0.009) 780 (11.1, 0.003) 807 (15.1, 0.002) oop(C=O)	764 s	775 w	770 w				768 (49.2, 0.009)	780 (11.1, 0.003)	807 (15.1, 0.002)	oop(C=O)
758 sh 758 m 761 w 748 m 747 w 745 m 754 (17.9, 0.26) 758 (22.3, 0.22) 755 (20.8, 0.12) v(C=S)	758 sh	758 m	761 w	748 m	747 w	745 m	754 (17.9, 0.26)	758 (22.3, 0.22)	755 (20.8, 0.12)	v(C=S)
727 m711 w726 m724 (0.2, 0.01)695 (2.2, 0.005)715 (0.03, 0.01) $\rho$ (C-H)		727 m		711 w	726 m		724 (0.2, 0.01)	695 (2.2, 0.005)	715 (0.03, 0.01)	$\rho$ (C—H)
677 m, br         657 m, br         685 w, br         644 w         695 (2.1, 0.003)         689 (9.1, 0.02)         695 (1.3, 0.02)         ρ(C-H, Ph)	677 m, br	657 m, br	685 w, br			644 w	695 (2.1, 0.003)	689 (9.1, 0.02)	695 (1.3, 0.02)	$\rho$ (C—H, Ph)
653 m         646 vw, br         643 w         631 vw         632 w         671 (16.1, 0.02)         678 (10.1, 0.03)         662 (24.6, 0.03)         ρ(N2-H)	653 m		646 vw, br	643 w	631 vw	632 w	671 (16.1, 0.02)	678 (10.1, 0.03)	662 (24.6, 0.03)	$\rho$ (N2—H)
631 vw         621 m         630 w         605 vw         621 w         611 (33.7, 0.02)         619 (5.5, 0.004)         634 (30.0, 0.02)         δ(C=O)	631 vw		621 m	630 w	605 vw	621 w	611 (33.7, 0.02)	619 (5.5, 0.004)	634 (30.0, 0.02)	$\delta$ (C=O)
609 w         601 m         606 w         614 w         606 w         610 (25.6, 0.02)         610 (36, 0.03)         607 (26.2, 0.001)         oop(C=S)	609 w	601 m	606 w	614 w		606 w	610 (25.6, 0.02)	610 (36, 0.03)	607 (26.2, 0.001)	oop(C=S)
599 s     594 sh     593 w     600 w     566 (5.5, 0.06)     606 (15.2, 0.06)     602 (16.3) $\rho(C-H)$	599 s	594 sh	593 w	600 w			566 (5.5, 0.06)	606 (15.2, 0.06)	602 (16.3)	$\rho(C-H)$
556 w, br         542 w         554 w         520 vw         564 (0.9, 0.007)         543 (12.7, 0.03)         528 (12.1)0.001         ρ(C-H)	556 w, br		542 w	554 w	520 vw		564 (0.9, 0.007)	543 (12.7, 0.03)	528 (12.1)0.001	$\rho(C-H)$
523 w         535 vw         510 m         532 (9.1, 0.01)         526 (4.1, 0.01)         523 (10.6, 0.002)         δ(CCC)	523 w	535 vw	510 m				532 (9.1, 0.01)	526 (4.1, 0.01)	523 (10.6, 0.002)	$\delta(CCC)$
506 w 503 vw 490 m 487 w 514 (8.8, 0.002) 508 (14.8, 0.01) 496 (26.6, 0.08) $\rho$ (C-H)	506 w	503 vw	490 m			487 w	514 (8.8, 0.002)	508 (14.8, 0.01)	496 (26.6, 0.08)	$\rho(C-H)$
470 w 470 $(3.1, 0.006)$ 463 $(4.80.02)$ 429 $(13.0, 0.007)$ $\delta$ (CCC)	470 w						470 (3.1, 0.006)	463 (4.80.02)	429 (13.0, 0.007)	$\delta(CCC)$
456 w         458 w         451 vw         463 (5.1, 0.02)         443 (5.1, 0.03)         427 (0.1, 0.02)         δ(CCC)	456 w			458 w	451 vw		463 (5.1, 0.02)	443 (5.1, 0.03)	427 (0.1, 0.02)	$\delta(CCC)$

^b Computed frequency and intensity values at the B3LYP/CBSB7 level of approximation. In parenthesis (IR, Raman) computed IR and Raman intensities (after transformation following ref [53]) in km/mol and Å4/amu. ^a FTIR of solid in KBr pellets. Band intensities and shape: vs = very strong; s = strong; m = medium; w = weak; espectively.

v: Stretching (subscripts s and as refer to symmetric and antisymmetric modes, respectively),  $\delta$ : deformation, ho: rocking, oop: out of plane deformation modes

packing of **1–3**, where molecules are linked to centro-symmetric dimers by intermolecular  $N-H\cdots$ S hydrogen bonds.

The molecular structures determined by using the B3LYP and B3PW91 hybrid functionals with moderate large basis sets (CBSB7 and  $6-311+G^*$ ) show excellent agreement with the experimental ones.

The IR and Raman spectra were analyzed with the assistance of the computed spectra and the main normal modes related with the thioamide group ("thioamide bands") were tentatively assigned. In particular, the NCN antisymmetric and symmetric stretching modes of the thiourea moiety (thioamide bands II and III, respectively) are assigned to the intense bands centered at around 1346 and 1146 cm⁻¹ in the infrared spectra of compounds **1–3**, respectively.

# 4. Experimental

#### 4.1. Synthesis and characterization

The 1-(4-Fluorobenzoyl)-3-(isomeric fluorophenyl) thioureas (1-3) were prepared by the reaction of 3-fluorobenzoyl isothiocyante produced in situ with isomeric fluoroanilines in excellent yields (Scheme 1). 2-Fluoroaniline, the 3-fluoroaniline and 4-fluoroaniline, potassium thiocyanate as well as 4-fluorobenzoyl chloride, were purchased from Aldrich and used as received. 4-Fluorobenzoyl chloride was treated in a 1:1 M ratio with potassium thiocyanate in dry acetonitrle to afford the 4-fluorobenzoyl isothiocyante intermediate which was not separated. Condensation of the latter with isomeric fluoroanilines furnished the 1-(3-fluorobenzoyl)-3-(substituted fluorophenyl)thiourea derivatives (1-3) in 60-84% yields. The melting points were recorded using a digital Gallenkamp (SANYO) model MPD.BM 3.5 apparatus and are as follows: (1), 110–111 °C, (2), 130–131 °C, (3), 138–139 °C. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 300 MHz and 75 MHz respectively with a Bruker 300 MHz spectrophotometer. Elemental analyses were conducted using a LECO-183 CHNS analyzer.

#### 4.2. Vibrational spectroscopy

Routine IR spectra were recorded on an IR Shimadzu 460 spectrophotometer as KBr pellets (Pakistan). Solid-phase IR spectra were recorded with a resolution of  $2 \text{ cm}^{-1}$  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  $2 \text{ cm}^{-1}$ .

#### 4.3. Quantum chemical calculations

All quantum chemical calculations were performed with the GAUSSIAN 03 program package [46]. The molecular geometries were optimized to standard convergence criteria by using the Becke three parameter hybrid functionals B3 [47] and the non-local correlation provided by LYP [48] and Perdew/Wang 91 [49] and Pople-type basis sets [50]. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found. Additionally, the CBSB7 basis set was used. The CBSB7 has the form 6-311G(2d,d,p) and has been developed by Petersson and coworkers as a part of the complete basis set CBS-QB3 energy compound method [51,52]. The Raman activities (in Å4/amu) calculated with the Gaussian 03 program were converted to relative Raman intensities [53].

Table 4				
Crvstal data	and structure	refinement fo	or compounds	1-3 ^a .

Compound	1	2	3
Formula weight	292.3	292.3	292.3
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P 2 ₁ /c	P 2 ₁ /n	P 2 ₁ 2 ₁ 2
a (Å)	8.4054(5)	16.024616	13.2613
b (Å)	12.0100(7)	4.3101(4)	24.823(5)
<i>c</i> (Å)	12.6211(8)	18.7829(19)	3.8140(8)
β (°)	90.601(1)	99.2242	
V (Å ³ )	1274.02(13)	1280.5(2)	1255.5(4)
Z	4	4	4
Dc (Mgm ⁻³ )	1.524	1.516	1.546
Absorp. coeff. $(mm^{-1})$	0.274	0.273	0.278
F (000)	600	600	600
Crystal size (mm ³ )	$0.43 \times 0.40 \times 0.32$	$0.39 \times 0.10 \times 0.09$	$0.39 \times 0.33 \times 0.27$
Data collection			
h	-11/10	-21/21	-17/16
k	-15/14	-5/5	-32/32
1	-16/16	-23/24	-4/5
Data collected	11,631	11,127	11,612
Unique reflections	3029	3048	2963
R (int)	0.019	0.063	0.107
Max./min. transm.	0.917/0.891	0.976/0.877	0.928/0.899
Parameters	182	181	181
GooF	1.019	1.038	1.035
Flack parameter	-	-	0.17(1)
R1[I > 2sigma(I)]	0.032	0.047	0.056
wR2 (all data)	0.089	0.111	0.116
max/min $\Delta F/e$ (Å ⁻³ )	0.29/-0.25	0.28/-0.25	0.32/-0.33
CCDC deposition numbers	784,075	784,076	784,077

^a Further conditions and refinement comments: Temperature 120(2) K, Wavelength 0.71073 Å, Theta ranges/° = 2.02–27.88, Absorption correction: Semi-empirical from equivalents, Refinement method: Full-matrix least-squares on  $F^2$ .

#### 4.4. X-ray data collection, structure solution and refinement

Crystals of the thioureas were grown by slow evaporation of 1:1 by volume acetone–anhydrous ethanol mixtures at room temperature. Pertinent crystal and refinement data for **1–3** are given in Table 4. Bruker-AXS SMART APEX CCD graphite monochromator,  $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å. Structures solved by direct methods, full-matrix least-squares refinement based on  $F^2$ . All but H atoms refined anisotropically [54]. Hydrogen atoms were located from difference Fourier maps and refined at idealized positions riding on the relevant carbon or nitrogen atoms with C—H = 0.95 and N—H = 0.88 Å and with isotropic displacement parameters U_{iso} (H) = 1.2U_{eq}(C, N).

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#### **Appendix A. Supplementary material**

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011. 05.051.

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