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Intra- and intermolecular hydrogen bonding and conformation in 1-acyl thioureas: An experimental and theoretical approach on 1-(2-chlorobenzoyl)thiourea

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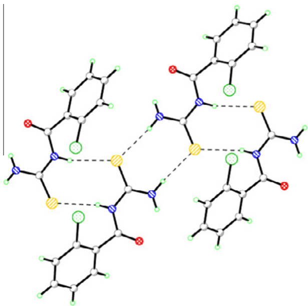
HIGHLIGHTS

- Crystal structures and vibrational properties were determined.
- The C=O and C=S double bonds of the acyl-thiourea group are mutually oriented in opposite directions.
- The $-NH_2$ is involved in strong N–H···O=C intramolecular hydrogen bond.
- Both, thioamide (N–H) and carbamide ($-NH_2$) groups participate in intermolecular N–H···S=C hydrogen bonds.
- Topological analysis reveals a Cl···N interaction playing a relevant role in crystal packing.

GRAPHICAL ABSTRACT



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ABSTRACT

The vibrational analysis (FT-IR and FT-Raman) for the new 1-(2-chlorobenzoyl)thiourea species suggests that strong intramolecular interactions affect the conformational properties. The X-ray structure determination corroborates that an intramolecular N–H···O=C hydrogen bond occurs between the carbonyl (–C=O) and thioamide ($-NH_2$) groups. Moreover, periodic system electron density and topological analysis have been applied to characterize the intermolecular interactions in the crystal. Extended N–H···S=C hydrogen-bonding networks between both the thioamide (N–H) and carbamide (NH_2) groups and the thiocarbonyl bond (C=S) determine the crystal packing. The Natural Bond Orbital (NBO) population analysis demonstrates that strong hyperconjugative remote interactions are responsible for both, intra and intermolecular interactions. The Atom in Molecule (AIM) results also show that the N–H···Cl intramolecular hydrogen bond between the 2-Cl-phenyl ring and the amide group characterized in the free molecule changes to an N···Cl interaction as a consequence of crystal packing.

Introduction

Very recently, Eccles at al. [1] demonstrate the versatility of the thioamide functional group [–C(S)NH_2] as a key moiety for crystal

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engineering. The related acetylthiourea species, CH_3-C(O)NHC(S)NH_2, has been known for more than a century [2] and represents the first example of the 1-acyl-thiourea family of compounds [–C(O)NHC(S)NH_2] [3–5]. Its X-ray structure was early reported [6], resulting in an molecular structure in which the heavy atoms skeleton are arranged in a planar fashion with the carbonyl double bond interacting *via* an intramolecular hydrogen bond with the –NH_2 group. The infrared and Raman spectra were also interpreted in terms of a C_S point group model [7]. More recent quantum chemical calculations on small model compounds [8] reveal that the central –C(O)NHC(S)NH_2 group can display several conformations, depending on the dihedral values around the acyl-N bond and the adjacent N–C bond [9].

For 1-(acyl/aroyl)-3-(mono-substituted) thiourea derivatives a local planar structure of the thiourea moiety is preferred, with opposite orientation between the C═O and C═S double bonds ("*S*-shape") [10]. In this conformation, a pseudo six-membered ring structure promotes a C═O···H–N intramolecular hydrogen bond. On the other hand, when the formation of a suitable hydrogen bond is prevented, as in 1-(acyl/aroyl)-3,3-(di-substituted) thiourea derivatives (R^2, $R^3 \neq$ H), the *anticlinal* geometry (*U* form) is preferred [11–14].

The understanding of the conformational properties on these compounds has direct relevance in applied fields, including chemosensors for selective and sensitive naked-eye recognition for anions [15–18] and new developments on biological [19] and pharmaceutical applications [20–22]. As has been recognized, the success of many of these applications of 1-acyl thioureas, rely on the formation of proper hydrogen bonds with particular receptors [23]. The 2-chlorophenylthiourea compound effectively coordinate zinc (II) cations in the presence of acetylacetonate forming a screw shaped square-pyramidal coordination compound with promising application in nonlinear optics [24].

Continuing our project dedicated to the study of 1-(acyl/aroyl)-3-(mono-substituted) thioureas [25,26], in this article the preparation of the new species 1-(2-chlorobenzoyl)thiourea is presented. It is interesting to note that although several thioureas containing the 1-(2-chlorobenzoyl) group with different degree of substitution at the second nitrogen atom have been reported [27–31], the non-substituted species remains unknown. In this work, the molecular and crystal structures in conjunction with the vibrational properties have been determined by X-ray diffraction and spectroscopic (infrared and Raman) analysis of the solid. These studied have been complemented by quantum chemical calculations. In particular the Natural Bond Orbital (NBO) [32,33] population analysis has been performed in order to evaluate the donor → acceptor intra and intermolecular interactions for the monomer and also for dimer and trimer arrangements of molecules. Finally, to better characterize the intermolecular interactions present in the crystal and the possible effect of packing in the intramolecular interactions, the topology of the electron density obtained from a periodic quantum calculation has been analyzed by using the atoms in molecules (AIM) approach [34].

Experimental

Synthesis and characterization

Following the method reported for related species [35], freshly prepared 2-chlorobenzoyl chloride was added to a solution of potassium thiocyanate in acetone to get the corresponding isothiocyanate *via* stirring at room temperature for 1 h. The *in situ* formed 2-chlorobenzoyl isothiocyanate was treated with aqueous ammonia at low temperature. On completion of the reaction mixture was poured in ice cold water and the solid product obtained was recrystallized from ethanol to afford yellow crystalline solid.

Yield: 85%; m.p: 152 °C; IR (cm^{-1}): 3329, 3153, 1687, 1236; ^{1}H-NMR (ppm, $CDCl_3$, 300 MHz): 11.64 (s, CON**H**, 1H), 9.64 (CSN**H₂**, 2H), 7.52 (m, 3H, Ar), 7.41(m, 1H Ar); ^{13}C-NMR ($CDCl_3$, 75 MHz): 182.0 (**C** = S), 167.7 (-**C**O), 135.0, 132.3, 130.31, 130.0; GC–MS: 139 (M^+), 111, 85, 75, 44; elemental analysis: Calcd. For $C_8H_7ClN_2OS$ C: 44.76, H: 3.29, N: 13.05, S: 14.94%. Found C: 44.70, H: 3.11, N: 13.02, S: 14.90%.

Instrumentation

Melting point was determined using a digital Gallenkamp (SANYO) model MPDBM3.5 apparatus and was uncorrected. ^{1}HNMR and ^{13}C NMR spectra were determined in $CDCl_3$with a 300 MHz Bruker AM-300 spectrophotometer. Mass Spectra (EI, 70 eV) were taken on a GC–MS, Agilent technologies 6890N with an inert mass selective detector 5973 mass spectrometer and elemental analyses were conducted using a LECO-183 CHNS analyzer.

Vibrational spectroscopy

Solid-phase (in 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. FTIR spectra (ATR) were recorded on an a Bio-Rad-Excalibur Series Mode FTS 3000 MX spectrophotometer. The FT-Raman spectra of the powdered solid sample 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

Molecular quantum chemical calculations have been performed with the GAUSSIAN 03 program package [36] by using the B3LYP DFT hybrid methods employing Pople-type basis set [37]. The moderate 6-31G(d,p) basis set has been applied for the relaxed scan calculations, whereas the extended valence triple-ξ basis set augmented with diffuse and polarization functions in both the hydrogen and weighty atoms [6-311++G(d,p)] has been used for geometry optimization and frequency calculations. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found. The recommended scale factor of 0.96 has been applied for analyzing the theoretical harmonic vibrational frequencies [38]. Periodic calculations were performed at the B3LYP/6-31G(d,p) level with Crystal98 and Crystal09 codes [39,40]. Using the experimental estimations as the starting point, the coordinates of the hydrogen atoms in the crystal were optimized to minimize the B3LYP/6-31G(d,p) crystal energy with heavy atom coordinates and cell parameters fixed at their experimental values. The topology of the resulting electron density was then analyzed using the TOPOND98 program [41]. For consistency with the periodic results, molecular and supramolecular electron densities were also analyzed with TOPOND98 from calculations performed with Crystal98 using geometry optimized with Crystal09.

X-ray data collection and structure refinement

X-ray data were collected on a STOE IPDS-II diffractometer with graphite-monochromated MoKα radiation. An empirical absorption correction with the PLATON program [42] was performed. The structure was solved by direct methods and refined with full-matrix least-squares on *F*2 using the program SHELXL97 [43]. H-atoms bonded to carbon atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. H-atoms bonded to N were freely refined. Full crystallographic data have been deposited with the Cambridge Crystal-