Structural study and spectroscopic investigations of N[3,5-Bis(trifluoromethyl) phenyl] thiourea

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ABSTRACT

The spectroscopic characterization of N[3,5-Bis(trifluoromethyl)phenyl]thiourea (BTU) was undertaken by FT-IR and FT-Raman spectroscopies, which was also used to interpreted in terms of fundamental bands. It is found that the experimental and the B3LYP/6-311G computed frequencies are in well agreement.

Keywords: FT-IR, FT-Raman, B3LYP

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I. INTRODUCTION

The last decade has seen the increasing use of thiourea derivatives as catalysts due to their hydrogen bonding interactions with partially developing negatively charged atoms in the substrates as well as in the transition states [1–3]. In parallel with well appreciated knowledge that hydrogen bonding plays a key role in the mode of action of various enzymes, well defined hydrogen bonding donors have started to serve as efficient catalysts for various organic transformations [4, 5]. Among others, N,N'-bis[3,5-bis(trifluoromethyl)phenyl]thiourea catalytic properties has been applied to a wide range of organic transformations [6–8]. In addition, incorporation of the 3,5-bis(trifluoromethyl)phenyl moiety into a chiral module has also become a common strategy for the design of novel chiral thiourea based catalysts [9]. Nowadays, merging Schreiner’s thiourea with another achiral catalytic species has paved a new way to further explore its potential applications [10]. This review summarizes the key developments of Schreiner’s thiourea including its proof of principle studies as well as its applications as catalyst and cocatalyst. Thiourea is important sulphur and nitrogen containing compounds that have proved to be useful substances in drug research in recent years.

In the present investigation, owing to the industrial and biological importance of BTU, the vibrational frequencies are determined using quantum chemical calculations (QCC). The structural parameters of the compound were also determined from ab initio HF and DFT/B3LYP methods with the standard 6-311G basis set and are discussed in detailed manner.

II. EXPERIMENTAL DETAILS

The pure sample of BTU was purchased from Lancaster chemical company, UK and used as such without any further purification to record Fourier transform Infrared (FT-IR) and Fourier transform-Raman (FT-Raman) spectra. The room temperature FT-IR spectrum of BTU measured in the 4000–400 cm⁻¹ region at a resolution of ± 1 cm⁻¹ using BRUKER IFS-66V Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and global arc source. The FT-Raman spectrum was recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The FT-Raman spectrum is recorded in the 3500–100 cm⁻¹ stokes region using the 1064 nm line of Nd:YAG laser for the excitation operating at 200mW power. The reported wavenumbers are expected to be accurate within ±1 cm⁻¹.
III. METHODS AND MATERIAL

In order to provide information with regard to the structural characteristics and the vibrational modes of BTU, the HF and B3LYP correlation functional calculations have been carried out. The entire calculations are performed using the GAUSSIAN 09W software package [11]. DFT employing the B3LYP keyword, which invokes Becke’s three-parameter hybrid method [12] using the correlation function of Lee et al. [13], implemented with 6-311G basis set. All the parameters are allowed to relax and all the calculations converged to an optimized geometry which corresponds to true minimum, as revealed by the lack of imaginary values in the wavenumber calculations. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry [14, 15]. Transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the total energy distribution (TED) are done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [16, 17]. The symmetry of the molecule is also helpful in making vibrational assignment. By combining the results of the GAUSSVIEW program [18, 19], the symmetry of the molecular considerations, vibrational frequency assignments are made with a high degree of confidence. There is always some ambiguity in defining internal coordinates. However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program. The systematic comparison of the results from density functional theory (DFT) theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumber.

IV. RESULTS AND DISCUSSION

4.1. Molecular Geometry

The optimized molecular structure of BTU is shown in Figure 1. The optimized geometrical parameters of BTU is obtained by HF and B3LYP methods with 6-311G basis set and are listed in the Table 1. According to the calculation the order of the bond length is C1–C2, C1–C6, C1–N12, C2–C3, C2–H7, C3–C4, C3–C11, C4–C5, C4–H8, C5–C6, C5–C10, C6–H9, C10–F19, C10–F20, C10–F21, C11–F22, C11–F23, C11–F24, N12–S16, N12–H13, N12–C14, C14–N15, C14–S16, N15–H17, N15–H18. From the order of the bond length, it is clear that the hexagonal structure of the benzene ring slightly distorted. This can be due to the influence of conjugation between the substituents and the ring.

Figure 1. Molecular structure of N[3,5- Bis(trifluoromethyl)phenyl] thiourea with atom numbering.

4.2. Vibrational Assignments

From the structural point of view the compound is assumed to have C1 point group symmetry and hence, all the calculated frequency transforming to the same symmetry species (A). The BTU molecule consists of 24 atoms and expected to have 66 normal modes of vibrations. The detailed vibrational assignments of fundamental modes of BTU along with the TED are reported in Table 2. The observed FT-IR and FT-Raman spectra of BTU are shown in Figures 2 and 3, respectively.

The main focus of the present investigation is the proper assignment of the experimental frequencies to the various vibrational modes of BTU in collaboration with the calculated vibrational frequencies at HF and B3LYP levels using the 6-311G basis set. The vibrational analysis obtained for BTU with the unscaled HF and B3LYP is generally somewhat different with the experimental values. These discrepancies can be
corrected either by computing anharmonic corrections explicitly or by introducing a scaled field or directly scaling the calculated wavenumbers with proper factor. A tentative assignment is often made on the basis of the unscaled frequencies by assuming the observed frequencies so that they are in the same order as the calculated ones. Then, for an easier comparison to the observed values, the calculated frequencies are scaled by the value of less than 1, to minimize the overall deviation. A better agreement between the computed and experimental frequencies can be obtained using different scale factors for different regions of vibrations. The resultant scaled frequencies are also listed in Table 2.

### 4.2.1. C–H vibrations

The molecular structure of BTU shows the presence of C–H stretching vibrations in the region 3100–3000 cm\(^{-1}\) and these vibrations are not found to be affected due to the nature and position of the substituent [20, 21]. Accordingly, in BTU compound the C–H stretching vibrations are observed at 3350, 3221 and 3000 cm\(^{-1}\) in the FT-IR spectrum whereas in the FT-Raman, it is observed at 3230 cm\(^{-1}\).

The C–H in-plane bending vibrations usually occur in the region 1430–990 cm\(^{-1}\) and is very useful for characterization. The FT-IR peaks observed at 990, 952 cm\(^{-1}\) and FT-Raman peaks observed at 975, 950 cm\(^{-1}\) are occurring due to the effect of C–H in-plane bending vibrations [22, 23]. C–H out-of-plane bending vibrations are occur in the region 900–667 cm\(^{-1}\). In BTU peaks obtained at 400 cm\(^{-1}\) in FT-IR confirms the C–H out-of-plane bending vibrations which agrees with the calculated values by B3LYP methods.

### 4.2.2. C–C vibrations

The bands observed at 1430–1670 cm\(^{-1}\) are assigned to C–C stretching modes [24]. Socrates [25] mentioned that the presence of conjugate substituent such as C–C causes a heavy doublet formation around the region 1625–1575 cm\(^{-1}\). The six ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands in the region 1660–1420 cm\(^{-1}\) [26]. As predicted in the earlier references, in BTU compound also there are prominent peaks at 1520 and 1500 cm\(^{-1}\) in FT-IR spectrum and peaks observed at 1690, 1530 and 1400 cm\(^{-1}\) in FT-Raman spectrum are assigned to C–C stretching vibrations. The C–C in-plane bending vibrations are appeared at 700 cm\(^{-1}\) in FT-IR spectrum and 900, 820, 800 and 700 cm\(^{-1}\) in FT-Raman and the out-of-plane bending vibrations are listed in Table 2. These assignments are in good agreement with the literature [27].

### 4.2.3. C–N Vibrations

The identification of C–N vibrations are a very difficult task, since the mixing of several modes are possible in the region. Silverstein et. al., [28] have assigned C–N stretching vibrations in the region 1382–1266 cm\(^{-1}\) for aromatic compounds. In the present study, the absorption band observed at 1330 and 1280 cm\(^{-1}\) in FT-
IR spectrum and 1360 and 1300 cm⁻¹ in FT-Raman spectrum are assigned to C–N stretching vibration for BTU. The in-plane and out-of-plane vibrations of the title compound are occurred within the characteristics region.

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Table 1. Optimized geometrical parameters of N[3,5–Bis(trifluoromethyl)phenyl]thiourea obtained by HF and B3LYP methods with 6-311G basis set.

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Table 2. Vibrational assignments of fundamental frequencies are obtained for N[3,5-Bis(trifluoromethyl)phenyl]thiourea using HF/6-311G and B3LYP/6-311G level of theories

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<td>890</td>
</tr>
<tr>
<td>35</td>
<td>874</td>
<td>778</td>
<td>865</td>
<td>693</td>
</tr>
<tr>
<td>36</td>
<td>795</td>
<td>747</td>
<td>784</td>
<td>679</td>
</tr>
</tbody>
</table>
Table 3. The Condensed Fukui functions ($f_k^+$), ($f_k^-$), ($f_k^\delta$) and dual descriptor $\Delta f(r)$ N[3,5-Bis (trifluoromethyl) phenyl] thiourea calculated by B3LYP/6-311G level of theory

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$f_k^+$</th>
<th>$f_k^-$</th>
<th>$f_k^\delta$</th>
<th>$\Delta f(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_1</td>
<td>0.0941</td>
<td>0.1062</td>
<td>0.0882</td>
<td>-0.0121</td>
</tr>
<tr>
<td>C_2</td>
<td>0.0066</td>
<td>-0.0812</td>
<td>-0.0455</td>
<td>-0.0878</td>
</tr>
<tr>
<td>C_3</td>
<td>-0.2592</td>
<td>-0.2576</td>
<td>-0.2505</td>
<td>0.0016</td>
</tr>
<tr>
<td>C_4</td>
<td>0.0564</td>
<td>-0.0557</td>
<td>-0.0086</td>
<td>-0.1121</td>
</tr>
<tr>
<td>C_5</td>
<td>-0.2653</td>
<td>-0.2675</td>
<td>-0.2657</td>
<td>0.0023</td>
</tr>
<tr>
<td>C_6</td>
<td>0.0126</td>
<td>-0.0729</td>
<td>-0.0313</td>
<td>-0.0855</td>
</tr>
<tr>
<td>H_1</td>
<td>0.2446</td>
<td>0.1599</td>
<td>0.1995</td>
<td>-0.0846</td>
</tr>
<tr>
<td>H_2</td>
<td>0.2554</td>
<td>0.1566</td>
<td>0.2036</td>
<td>-0.0988</td>
</tr>
<tr>
<td>H_3</td>
<td>0.3513</td>
<td>0.3130</td>
<td>0.3374</td>
<td>-0.0383</td>
</tr>
<tr>
<td>C_9</td>
<td>0.8061</td>
<td>0.7501</td>
<td>0.7779</td>
<td>-0.0560</td>
</tr>
<tr>
<td>C_10</td>
<td>0.8196</td>
<td>0.7508</td>
<td>0.7861</td>
<td>-0.0688</td>
</tr>
<tr>
<td>N_12</td>
<td>-0.4907</td>
<td>-0.5686</td>
<td>-0.5443</td>
<td>0.0779</td>
</tr>
<tr>
<td>H_13</td>
<td>0.3634</td>
<td>0.2934</td>
<td>0.3324</td>
<td>-0.0701</td>
</tr>
<tr>
<td>C_14</td>
<td>-0.0157</td>
<td>-0.0618</td>
<td>-0.0221</td>
<td>0.0461</td>
</tr>
<tr>
<td>N_15</td>
<td>-0.7630</td>
<td>-0.8124</td>
<td>-0.8050</td>
<td>0.0494</td>
</tr>
<tr>
<td>S_16</td>
<td>0.4246</td>
<td>-0.3229</td>
<td>0.0779</td>
<td>-0.7475</td>
</tr>
<tr>
<td>H_17</td>
<td>0.3962</td>
<td>0.3143</td>
<td>0.3592</td>
<td>-0.0818</td>
</tr>
<tr>
<td>H_18</td>
<td>0.4078</td>
<td>0.3123</td>
<td>0.3677</td>
<td>-0.0955</td>
</tr>
<tr>
<td>F_19</td>
<td>-0.2458</td>
<td>-0.2703</td>
<td>-0.2596</td>
<td>0.5162</td>
</tr>
<tr>
<td>F_20</td>
<td>-0.2402</td>
<td>-0.2737</td>
<td>-0.2590</td>
<td>0.5140</td>
</tr>
<tr>
<td>F_21</td>
<td>-0.2389</td>
<td>-0.2803</td>
<td>-0.2607</td>
<td>0.5192</td>
</tr>
<tr>
<td>F_22</td>
<td>-0.2475</td>
<td>-0.2797</td>
<td>-0.2642</td>
<td>0.5272</td>
</tr>
<tr>
<td>F_23</td>
<td>-0.2307</td>
<td>-0.2716</td>
<td>-0.2521</td>
<td>0.5023</td>
</tr>
<tr>
<td>F_24</td>
<td>-0.2418</td>
<td>-0.2801</td>
<td>-0.2612</td>
<td>0.5219</td>
</tr>
</tbody>
</table>
4.2.4. CF₃ Vibrations

Usually symmetric and antisymmetric CF₃ stretching vibrations are in the ranges 1290–1235 and 1226–1200 cm⁻¹, respectively [29, 30]. Therefore the band located at 1240 cm⁻¹ in FT-IR spectrum is assigned to symmetric stretching vibrations. C–F deformations usually occur in regions 690–631 cm⁻¹, 640–580 cm⁻¹ and 570–510 cm⁻¹ [25]. Accordingly CF₃ ipb is identified at 600 cm⁻¹ in FT-Raman spectrum. CF₃ rocking vibrational frequency ranges at 460–350 cm⁻¹ [31]. In the present study, the CF₃ ipr bands observed at 535, 510 cm⁻¹ in FT-Raman spectrum.

5. Fukui Function

Density Functional Theory (DFT) is a powerful tool for the study of reactivity and selectivity in a molecule. Chemical potential, hardness and softness are the global properties related to the chemical reactivity, whereas local reactivity is related to selectivity concept. The most important local reactivity parameter is the Fukui function. The Fukui function for a molecule has been defined as the derivative of electron density with respect to the change of number of electrons, keeping the positions of nuclei unchanged [32, 33]. Fukui function gives us information about a highly electrophilic/nucleophilic center in a molecule. In practice a convenient way of calculating the Fukui functions at atomic resolution is to use the condensed Fukui functions [34]. The condensed Fukui function \( f_k^+ \) for nucleophilic attack, \( f_k^- \) for electrophilic attack and \( f_k^0 \) for free radical attack can be expressed as:

\[
\begin{align*}
  f_k^+ &= q_k (N + 1) - q_k (N) \\
  f_k^- &= q_k (N) - q_k (N - 1) \\
  f_k^0 &= (q_k(N+1) - q_k(N-1))/2
\end{align*}
\]

where \( q_k \) is the electronic population of atom k in the neutral (N), anionic (N+1) or cationic (N-1) chemical species. In the present study the electronic population was calculated by natural population analysis (NPA). Morrel et al. [35] have proposed a new dual descriptor \( \Delta f(r) \) for nucleophilicity and electrophilicity. It is defined as the difference between the nucleophilic and electrophilic Fukui function and is given by the equation:

\[
\Delta f(r) = [f_k^- - f_k^+]
\]

If \( \Delta f(r) > 0 \), then the site is electrophilic, if \( \Delta f(r) < 0 \), then the site is nucleophilic. Dual descriptor provides a positive value for site prone to nucleophilic attack and a negative value for site prone to electrophilic attack. For BTU C₁, C₂, C₄, C₆, H₂, H₈, H₉, C₁₀, C₁₁, H₁₃, S₁₆, H₁₇ and H₁₈ are prone to electrophilic attack whereas C₃, C₅, N₁₂, C₁₄, N₁₅, F₁₉, F₂₀, F₂₁, F₂₂, F₂₃ and F₂₄ are prone for nucleophilic attack. The condensed Fukui functions \( (f_k^+) \), \( (f_k^-) \), \( (f_k^0) \) and dual descriptor \( \Delta f(r) \) of BTU are given in Table 4.

V. CONCLUSION

HF and B3LYP methods with the 6-311G basis set were utilized a detailed study of the structure, geometrical parameters and vibrational frequencies of BTU. The observed spectra of title compound were found to be in good agreement with B3LYP/6-311G level of calculated values. The Fukui function calculations showed that the amino group nitrogen atom and sulfur are the most probable sites for electrophilic and free radical attacks.

VI. REFERENCES


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[22]. Vijayakumar G Saravanan N 2016 Elixir Comp. Chem. 93 39522.


