

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

L. Bhuvanewari^{*a}, U. Sankar^b, S. MeenakshiSundar^c, K. Parimala^d

^aDepartment of Physics, N.K.R.Government Arts College for women, Namakkal, India

^bDepartment of Physics, Sri K.G.S. Arts College, Srivaikuntam, India.

^cDepartment of Physics, Sri Paramakalyani College, Alwarkurichi, India.

^dDepartment of Physics, Vivekanandha College of Arts and Sciences for Women, Namakkal, India.

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

*Corresponding author: L. Bhuvanewari (labhuvana178@gmail.com)

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 $\pm \text{cm}^{-1}$ 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 $\pm 1 \text{ cm}^{-1}$.

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.

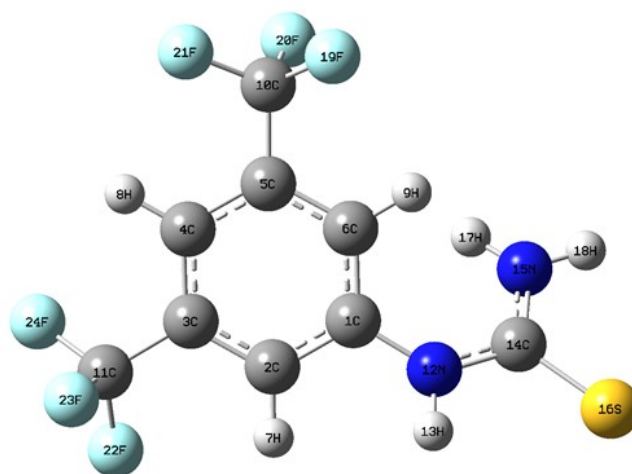


Figure 1. Molecular structure of N[3,5-Bis(trifluoromethyl)phenyl] thiourea with atom numbering.

4.2. Vibrational Assignments

From the structural point of view the compound is assumed to have C_1 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.

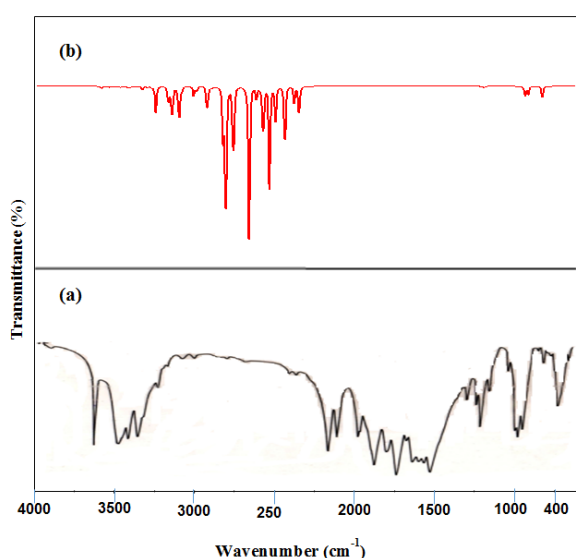


Figure 2. Experimental (a) and calculated (b) FT-IR spectra of N[3,5-Bis(trifluoromethyl) phenyl] thiourea.

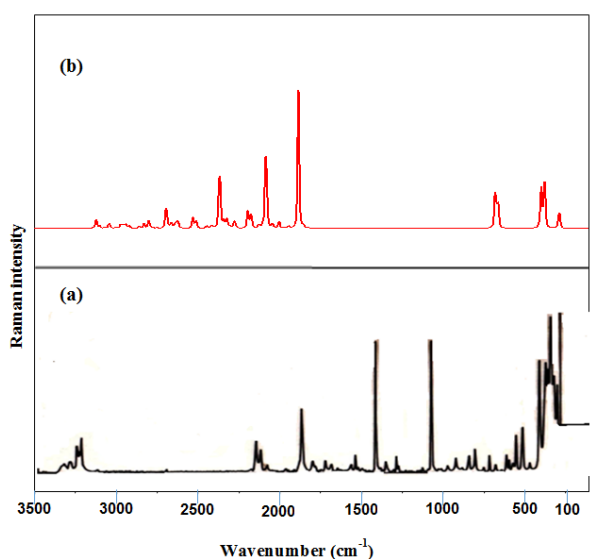


Figure 3. Experimental (a) and calculated (b) FT-Raman spectra of N[3,5-Bis(trifluoromethyl)phenyl] thiourea.

4.2.1. C–H vibrations

The molecular structure of BTU shows the presence of C–H stretching vibrations in the region $3100\text{--}3000\text{ cm}^{-1}$ 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 occurs in the region $1430\text{--}990\text{ cm}^{-1}$ 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 $900\text{--}667\text{ cm}^{-1}$. 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 $1430\text{--}1670\text{ cm}^{-1}$ 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 $1625\text{--}1575\text{ cm}^{-1}$. The six ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands in the region $1660\text{--}1420\text{ cm}^{-1}$ [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 $1382\text{--}1266\text{ cm}^{-1}$ 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.

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

Bond lengths (Å)	Values		Bond angles (°)	Values		Dihedral angles (°)	Values	
	HF	B3LYP		HF	B3LYP		HF	B3LYP
C1–C2	1.385	1.403	C2–C1–C6	119.757	119.210	C6–C1–C2–C3	0.199	0.665
C1–C6	1.387	1.401	C2–C1–N12	120.140	118.553	C6–C1–C2–H7	-179.997	179.466
C1–N12	1.424	1.414	C6–C1–N12	120.090	122.173	N12–C1–C2–C3	178.999	177.841
C2–C3	1.386	1.393	C1–C2–C3	119.883	120.103	N12–C1–C2–H7	-1.196	-3.357
C2–H7	1.069	1.080	C1–C2–H7	119.365	119.862	C2–C1–C6–C5	0.235	-1.604
C3–C4	1.382	1.397	C3–C2–H7	120.755	120.023	C2–C1–C6–H9	179.344	175.967
C3–C11	1.489	1.493	C2–C3–C4	120.707	121.056	N12–C1–C6–C5	-178.566	-178.673
C4–C5	1.384	1.393	C2–C3–C11	118.804	119.495	N12–C1–C6–H9	0.543	-1.101
C4–H8	1.067	1.078	C4–C3–C11	120.446	119.393	C2–C1–N12–H13	-88.594	-36.395
C5–C6	1.384	1.397	C3–C4–C5	119.066	118.496	C2–C1–N12–C14	91.618	146.464
C5–C10	1.489	1.493	C3–C4–H8	120.476	120.749	C6–C1–N12–H13	90.201	140.692
C6–H9	1.069	1.078	C5–C4–H8	120.456	120.754	C6–C1–N12–C14	-89.584	-36.448
C10–F19	3.583	2.625	C4–C5–C6	120.731	121.321	C1–C2–C3–C4	-0.416	0.628
C10–F20	1.362	1.398	C4–C5–C10	119.947	120.089	C1–C2–C3–C11	-178.080	-176.681
C10–F21	1.368	1.404	C6–C5–C10	119.254	118.536	H7–C2–C3–C4	179.783	-178.171
C11–F22	1.361	1.393	C1–C6–C5	119.851	119.789	H7–C2–C3–C11	2.119	4.519
C11–F23	1.364	1.397	C1–C6–H9	119.357	120.324	C2–C3–C4–C5	0.192	-0.957
C11–F24	1.366	1.402	C5–C6–H9	120.785	119.841	C2–C3–C4–H8	-179.616	179.165
C12–F16	1.361	1.396	C5–C10–F19	112.211	112.355	C11–C3–C4–C5	177.817	176.355
N12–H13	0.991	1.008	C5–C10–F20	111.880	111.629	C11–C3–C4–H8	-1.991	-3.521
N12–C14	1.352	1.380	C5–C10–F21	112.379	112.828	C2–C3–C11–F22	-44.832	-28.594
C14–N15	1.333	1.355	F19–C10–F20	106.197	105.872	C2–C3–C11–F23	74.292	90.904
C14–S16	1.731	1.721	F19–C10–F21	107.295	107.222	C2–C3–C11–F24	-165.520	-149.540
N15–H17	0.989	1.006	F20–C10–F21	106.469	106.482	C4–C3–C11–F22	137.497	154.051
N15–H18	0.988	1.004	C3–C11–F22	111.970	112.392	C4–C3–C11–F23	-103.378	-86.450
			C3–C11–F23	112.091	112.001	C4–C3–C11–F24	16.808	33.105
			C3–C11–F24	112.402	112.379	C3–C4–C5–C6	0.248	-0.004
			F22–C11–F23	106.112	106.224	C3–C4–C5–C10	177.238	177.308
			F22–C11–F24	107.157	107.134	H8–C4–C5–C6	-179.942	179.87
			F23–C11–F24	106.703	106.276	H8–C4–C5–C10	-2.953	-2.814
			C1–N12–H13	118.384	117.203	C4–C5–C6–C1	-0.463	1.289
			C1–N12–C14	126.468	129.629	C4–C5–C6–H9	-179.558	-176.294
			H13–N12–C14	115.147	113.114	C10–C5–C6–C1	-177.473	-176.065
			N12–C14–N15	117.339	117.362	C10–C5–C6–H9	3.431	6.351
			N12–C14–S16	120.506	120.133	C4–C5–C10–F19	145.937	143.655
			N15–C14–S16	122.153	122.499	C4–C5–C10–F20	-94.807	-97.581
			C14–N15–H17	123.381	123.218	C4–C5–C10–F21	24.912	22.291
			C14–N15–	118.203	117.564	C6–C5–C10–F19	-37.027	-38.957

			H18					
			H17-N15-H18	118.413	118.309	C6-C5-C10-F20	82.226	79.806
						C6-C5-C10-F21	-158.054	-160.321
						C1-N12-C14-N15	-0.286	-12.692
						C1-N12-C14-S16	179.695	168.086
						H13-N12-C14-N15	179.921	170.074
						H13-N12-C14-S16	-0.097	-9.148
						N12-C14-N15-H17	-0.343	-11.186
						N12-C14-N15-H18	-179.986	179.919
						S16-C14-N15-H17	179.675	168.014
						S16-C14-N15-H18	0.032	-0.878

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

Sl.No.	Observed frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹)				Assignments with >10 % of TED
	FT-IR	FT-Raman	HF		B3LYP		
			Unscaled	Scaled	Unscaled	Scaled	
1	3600(vs)		3967	3736	3718	3578	NH2 sym (100)
2	3500(vw)		3851	3692	3601	3431	NH asym (99)
3	3415(w)		3627	3516	3574	3378	vN-H (99)
4	3350(m)		3399	3243	3332	3102	vC-H (99)
5	3221(vw)	3230(vw)	3279	3137	3220	3081	vC-H (98)
6	3000(vw)		3209	3069	3108	3058	vC-H (97)
7		1690(s)	1839	1784	1691	1628	vC-C (97)
8			1711	1622	1653	1614	vC-C (96)
9			1604	1508	1650	1607	vC-C (95)
10	1520(w)	1530(vw)	1696	1584	1574	1506	vC-C (93)
11	1500(w)		1617	1478	1497	1583	vC-C (96)
12			1604	1459	1493	1462	vC-C (90)
13			1582	1399	1445	1394	vC-C (94)
14		1400(vs)	1521	1345	1394	1338	vC-C (93)
15		1360(vw)	1460	1288	1369	1279	vC-N (92)
16	1330(vw)	1300(vw)	1422	1272	1338	1270	vC-N (91)
17	1280(vw)		1406	1247	1280	1243	vC-N (90)
18		1260(w)	1348	1223	1272	1207	vC-S (94)
19	1240(vs)		1326	1201	1249	1193	CF ₃ sym (89)
20			1298	1183	1149	1173	CF ₃ sym (90)
21			1267	1161	1141	1157	CF ₃ asym (88)
22			1243	1146	1107	1141	CF ₃ asym (87)
23			1221	1105	1084	1096	CF ₃ asym (86)
24			1223	1093	1079	1085	CF ₃ asym (85)
25	1060(vw)		1189	1062	1067	1048	bN-H (84)
26		1050(vs)	1157	1053	1046	1027	NH2 sciss (83)
27	1000(vw)		1106	1026	1027	1008	NH rock (82)
28	960(vw)		1100	1005	995	966	bC-H (81)
29			1093	987	979	958	bC-H (80)
30		930(vw)	1066	965	955	933	bC-H (79)
31		900(w)	1002	944	932	922	bC-C (78)
32		820(vw)	921	898	914	837	bC-C (77)
33		800(w)	908	881	903	812	bC-C (76)
34	700(vw)	700(vw)	897	788	890	717	bC-C (75)
35			874	778	865	693	bC-C (74)
36			795	747	784	679	bC-N (73)

37			770	741	761	668	bC-N (72)
38			728	714	723	645	bC-N (71)
39			715	703	708	639	bC-S (70)
40			707	695	698	631	bCF ₃ ipb (69)
41		600(vw)	672	672	685	608	bCF ₃ ipb (68)
42			651	636	637	598	bCF ₃ sb (67)
43			640	612	619	565	bCF ₃ sb (66)
44		535(m)	582	603	607	528	bCF ₃ ipr (65)
45		510(m)	546	597	596	499	bCF ₃ ipr (64)
46		490(vw)	585	539	580	485	ωN-H (63)
47			570	519	561	465	NH ₂ wagg (62)
48			557	498	552	440	NH twist (61)
49	400(vs)		539	475	531	428	ωC-H (60)
50			531	428	523	393	ωC-H (59)
51			510	418	502	382	ωC-H (58)
52			480	379	475	336	ωC-C (57)
53		300(s)	422	342	427	309	ωC-C (56)
54			402	321	397	286	ωC-C (55)
55			346	302	338	279	ωC-C (54)
56		250(vs)	332	279	324	262	ωC-C (53)
57			310	258	302	241	ωC-N (52)
58		200(vs)	292	209	287	203	ωC-N (51)
59			260	160	256	191	ωC-N (40)
60			222	138	217	156	ωC-S (38)
61			173	119	165	133	CF ₃ opr (30)
62			143	96	135	112	CF ₃ opr(27)
63			134	83	126	95	CF ₃ opb (35)
64			114	62	109	74	CF ₃ opb (29)
65			97	41	95	39	tCF ₃ (25)
66			78	25	76	15	tCF ₃ (24)

Table 3. The Condensed fukui functions (f_k^+), (f_k^-), (f_k^0) and dual descriptor $\Delta f(r)$ N[3,5-Bis (trifluoromethyl) phenyl] thiourea calculated by B3LYP/6-311G level of theory

Atoms	f_k^+	f_k^-	f_k^0	$\Delta f(r)$
C ₁	0.0941	0.1062	0.0882	-0.0121
C ₂	0.0066	-0.0812	-0.0455	-0.0878
C ₃	-0.2592	-0.2576	-0.2505	0.0016
C ₄	0.0564	-0.0557	-0.0086	-0.1121
C ₅	-0.2653	-0.2675	-0.2657	0.0023
C ₆	0.0126	-0.0729	-0.0313	-0.0855
H ₇	0.2446	0.1599	0.1995	-0.0846
H ₈	0.2554	0.1566	0.2036	-0.0988
H ₉	0.3513	0.3130	0.3374	-0.0383
C ₁₀	0.8061	0.7501	0.7779	-0.0560
C ₁₁	0.8196	0.7508	0.7861	-0.0688
N ₁₂	-0.4907	-0.5686	-0.5443	0.0779
H ₁₃	0.3634	0.2934	0.3324	-0.0701
C ₁₄	-0.0157	-0.0618	-0.0221	0.0461
N ₁₅	-0.7630	-0.8124	-0.8050	0.0494
S ₁₆	0.4246	-0.3229	0.0779	-0.7475
H ₁₇	0.3962	0.3143	0.3592	-0.0818
H ₁₈	0.4078	0.3123	0.3677	-0.0955
F ₁₉	-0.2458	-0.2703	-0.2596	0.5162
F ₂₀	-0.2402	-0.2737	-0.2590	0.5140
F ₂₁	-0.2389	-0.2803	-0.2607	0.5192
F ₂₂	-0.2475	-0.2797	-0.2642	0.5272
F ₂₃	-0.2307	-0.2716	-0.2521	0.5023
F ₂₄	-0.2418	-0.2801	-0.2612	0.5219

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:

$$f_k^+ = q_k(N+1) - q_k(N)$$

$$f_k^- = q_k(N) - q_k(N-1)$$

$$f_k^0 = (q_k(N+1) - q_k(N-1))/2$$

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, H₇, 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

- [1]. Zhang Z and Schreiner P R 2009 Chem. Soc. Rev. 38 1187-1198.
- [2]. Kotke M and Schreiner P R 2009 in Hydrogen Bonding in Organic Synthesis, ed. P. M. Pihko, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 141-351.
- [3]. Hof K Lippert K M and Schreiner P R 2011 in Science of Synthesis-Asymmetric Organocatalysis, ed. K. Maruoka, Thieme, Stuttgart 297-412.
- [4]. Yu X H and Wang W 2008 Chem. Asaian J. 3 516-532.
- [5]. Doyle A G and Jacobsen E N 2007 Chem. Rev. 107 5713-5743.
- [6]. Wittkopp A and Schreiner P R 2003 Chem. Eur. J. 9 407-414.
- [7]. Schreiner P R 2003 Chem. Soc. Rev. 32 289-296.
- [8]. Schreiner P R and Wittkopp A 2002 Org. Lett. 4 217-220.
- [9]. Cannon S J 2009 Synlett. 8 354-376.
- [10]. Hrdina R Müller C E Wende R C Lippert K M Benassi M Spengler B and Schreiner P R 2011 J. Am. Chem. Soc. 133 7624-7627.
- [11]. Frisch M J et al. 2009 GAUSSIAN 98, Revision A 11.4, Gaussian, Inc, Pittsburgh PA.
- [12]. Becke A D 1993 J. Chem. Phys. 98 5648.
- [13]. Lee C Yang W and Parr R G 1988 Phys. Rev. B 37 785.
- [14]. Pulay P Fogarasi G Pongor G Boggs J E and Vargha A 1983 J. Am. Chem. Soc. 105-7037.
- [15]. Rauhut G and Pulay P 1995 J. Phys. Chem. 99 3093.

- [16]. Sundius T 1990 J. Mol. Struct, 218 321 (MOLVIB (V.7.0): Calculation of Harmonic Force Fields and Vibrational Modes of Molecules, QCPE program No.807 (2002).
- [17]. Sundius T 2002 Vib. Spectrosc. 29 89.
- [18]. Fogarai G Zhou X Taylor P W and Pulay P 1992 J. Am. Chem. Soc. 114 8191.
- [19]. Florian J and Johnson B G 1994 J. Chem. Phys. 98 3681.
- [20]. Senthil Kumar R and Marudhaiveeran N 2015 Elixir.vib. spec. 87 35682.
- [21]. Sharma Y R 1994 Elementary Organic Spectroscopy - Principles and Chemical Applications, S. Chand & Company Ltd., New Delhi 92.
- [22]. Vijayakumar G Saravanan N 2016 Elixir Comp. Chem. 93 39522.
- [23]. Vien L Colthup N B Fateley W G and Grassell J G 1991 The Handbook of Infrared Raman
- [24]. Characteristic Frequencies of Organic Molecules, Academic Press, Boston, MA.
- [25]. Sathyanarayana D N 2004 Vibrational Spectroscopy - Theory and Applications, Second ed. New Age International (P) Limited Publishers, New Delhi.
- [26]. Socrates G 2001 Infrared and Raman, Characteristics Group Frequencies, 3rd edition, Wiley, New York.
- [27]. Dani V R, 1995 Organic Spectroscopy, Tata-McGraw Hill Publishing Company, New Delhi, 139.
- [28]. Balachandran V and Parimala K 2013 Spectrochim. acta A 102 30-51.
- [29]. Silverstein R M Clayton Basseler G and Morrill T C 1991 Spectrometric identification of Organic Compounds, John Wiley and Sons, New York.
- [30]. Fernandez L E Benaltabef A Navarro A Fernandez Gomez M and Varette E L 2000 Spectrochim. Acta A 56 1101.
- [31]. Fernandez L E Ben Altabet A and Varette E L 2002 J. Mol. Struct. 612.
- [32]. Gounev T K Guirgis A and Durig J R 1997 J. Mol. Struct. 613 436-437.
- [33]. Ayers P W and Parr R G 2000 J. Am. Chem. Soc. 122 2010-2018.
- [34]. Parr R G and Yang W J 1984 Am. Chem. Soc. 106 511-516.
- [35]. Yang W and Mortier W J J 1986 Am. Chem. Soc. 108 5708-5711.
- [36]. Morell C Grand A and Toro-Labbe A 2005 J. Phys. Chem. A 109 205-212.