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Structural, spectral, optical and antimicrobial properties of synthesized 1-benzoyl-3-furan-2-ylmethyl-thiourea

Fatma Karipcin [a], Murat Atis [b,*], Bahtiyar Sariboga [c], Hasan Celik [a], Murat Tas [d]

[a] Department of Chemistry, Sciences and Arts Faculty, Nevsehir University, 50300 Nevsehir, Turkey
[b] Department of Physics, Sciences and Arts Faculty, Nevsehir University, 50300 Nevsehir, Turkey
[c] School of Health, Sinop University, 57000 Sinop, Turkey
[d] Department of Chemistry, Sciences and Arts Faculty, Giresun University, 28100 Giresun, Turkey

HIGHLIGHTS

- The 1-benzoyl-3-furan-2-ylmethyl-thiourea synthesized.
- The FT-IR, ^{13}C, ^{1}H NMR and X-ray used for characterization.
- The B3LYP method with the standard 6-311++G(d,p) basis sets used to calculation.
- The nonlinear optical properties are investigated theoretically.
- Bftu exhibited antimicrobial activity against, *L. monocytogenes, B. cereus* and *S. aureus*.

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ABSTRACT

The 1-benzoyl-3-furan-2-ylmethyl-thiourea **(bftu)** was synthesized and its structure was determined by elemental analyses, IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and single crystal X-ray diffraction analysis. Also its antimicrobial activity was determined. We analyzed the optimized geometric structure and energies of **bftu** in the ground state as theoretically. Theoretical calculations were performed at the DFT level. Selected experimental bands were assigned and characterized on the basis of the scaled theoretical wavenumbers by their total energy distribution (TED). The nuclear magnetic resonance (NMR) chemical shifts of **bftu** molecule were calculated using the gauge-invariant-atomic orbital (GIAO) method in acetone solution and compared with the experimental data. The dipole moment, linear polarizability and first hyper polarizability values were also computed.

1. Introduction

Thiourea and its derivatives have been widely used in research and technological applications such as for extraction of toxic metals using a solid supported liquid membrane system [1,2], as catalysts in chemical reactions [3–6], as receptors for anion and cation detection [7,8]. Due to nonlinear optical properties, single crystals of thiourea are being extensively employed in the electronic industry, for example, as polarization filters, electronic light shutters, electronic modulators, and as components in electro-optic and electro-acoustic devices [9–11]. Thiourea and substituted thioureas are furthermore widely used as additives in various electrochemical processes [12,13].

The thiourea derivatives represent one of the most promising classes of anticancer agents because of their good inhibitory activity against protein tyrosine kinases (PTKs) [14,15], human sirtuin type proteins 1 and 2 (SIRT1 and SIRT2) [16], topoisomerase II [17] and DNA repair synthesis [18]. In addition, thiourea derivatives also exhibit other various biological properties such as antiviral, antimalarial, antibacterial, antiinflammatory, insecticidal, herbicidal, rodenticidal and plant-growth properties [19–25].

The presence of hard O- and N- and soft S-donor atoms in the backbones of these ligands enable them to react readily with both transition group and main group metal ions, yielding stable metal complexes. In general, thiourea derivative ligands consist some substituents with different electron-donating or electron withdrawing groups and, therefore, may have interesting electrochemical properties. Some of which have been shown to exhibit interesting physico-chemical properties and significant biological activities [25–28]. Therefore, researchers pay a great interest in their synthesis, structure, biological activity and application of this kind of compounds.

* Corresponding author. Tel.: +90 384 228 1100; fax: +90 384 215 3948.
E-mail address: atis@nevsehir.edu.tr (M. Atis).

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N-benzoyl-N′-arylthioureas have been thoroughly investigated in connection with the formation of intramolecular hydrogen bonding [29–31]. Bifunctionality of amine–thiourea compounds carries the possibility of intra- and intermolecular interactions via hydrogen bonding. In effect, it was found that the intramolecular hydrogen bond between the oxygen atom in the C=O group and the hydrogen atom of the thiourea group is favored [30,31]. The intramolecular H-bond observed in these compounds is in agreement with Etter's hydrogen bond rules, which indicate that if six-membered ring intramolecular hydrogen bonds can form, they will usually do so in preference to forming intermolecular hydrogen bonds [32]. Another rule states that the best proton donors and acceptors remaining after intramolecular hydrogen bond formation form intermolecular hydrogen bonds to one another [33]. Moreover, the hydrogen-bonding ability of the thiourea moiety has extensively been used in the construction of anion receptors [31,33] and in the thiourea-based metal complexes [25–28] and organocatalysts [3–5].

By means of increasing development of computational chemistry in the past decade, the research on theoretical modeling of drug design, functional material design, etc., has become much more mature than ever. Many important chemical and physical properties of biological and chemical systems can be predicted from the first principles of various computational techniques [34]. With the development of computer hardware, software, and computational methods, it is possible to correctly describe the physicochemical properties of relatively small molecules from the first principles [34–36]. In conjunction with the development of technology, among the computational methods calculating the electronic structure of molecular systems, Density Functional Theory (DFT) has been used extensively to calculate a wide variety of molecular properties such as equilibrium structure, charge distribution, UV–visible, FTIR and NMR spectra, and provided reliable results which are in accordance with experimental data [37–39]. The literature survey revealed that the DFT has a great accuracy in reproducing the experimental values in terms of geometry, dipole moment, vibration frequency, and so on [38–41].

Concerning with the above mentioned phenomena, we present here the synthesis, crystallographic, spectroscopic studies of the newly synthesized thiourea derivative ligand, 1-benzoyl-3-furan-2-ylmethyl-thiourea, as well as the theoretical studies on it by using DFT/6-311++G(d,p) method. Additionally, the ground state theoretical geometrical parameters of title molecule were calculated. Moreover, the dipole moment, nonlinear optical (NLO) properties has also been studied. We also make comparisons between experiments and calculations.

2. Experimental

2.1. Materials and physical measurements

All reagents used in this study were reagent grade and used without further purification. Acetone was dried and used freshly distilled prior to use.

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectrum of the compound was registered using a Perkin Elmer Spectrum 100 FT-IR spectrometer (4000–650 cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 High Resolution Console, using *d*-acetone as the solvent and TMS as an internal standard. C, H, N and S analyses were carried out on a LECO 932 CHNS analyzer. Melting point was determined using an EZ-Melt melting point apparatus and was uncorrected.

Single crystal X-ray data were collected on an Agilent SuperNova diffractometer with an Eos CCD detector using Mo Kα radiation (λ = 0.71073 Å). The CrysAlisPro software program was used for data collection, cell refinement and data reduction. Using Olex2 [42], the structure was solved by the ShelXS [43] structure solution program by direct methods and refined with the ShelXL [44] refinement package using least-squares minimization. To prepare material for publication Mercury 3.0 were used. All H atoms were refined using a riding model. The details of the X-ray data collection, structure solution and structure refinement are given in Table 1. Selected bond distances and angles are listed in Table 2.

2.1.1. Synthesis

1-Benzoyl-3-furan-2-ylmethyl-thiourea was prepared by a procedure similar to that reported in the literature [26,33,45]. A solution of benzoyl chloride (20 mmol; 2.80 g) in dry acetone (10 mL) was added dropwise to a solution of ammonium thiocyanate (20 mmol; 1.52 g) in dry acetone (30 mL) under stirring. The reaction mixture was heated (40 °C) under reflux for 1 h, and then cooled to room temperature. The formed precipitate of NH_4Cl was filtered off. A solution of furfurylamine (22 mmol; 2.14 g) in dry acetone (20 mL) was slowly added to the resulting solution, which then was stirred for 2 h. Afterwards the mixture was filtered into a beaker containing some ice. The resulting white precipitate was washed with distilled water followed by MeOH and diethylether (yield 63%). Re-crystallization from methanol yielded colorless crystals suitable for X-ray analysis.

Colorless crystals. Yield: 63%. Mp: 117 °C. Anal. Calcd. for $C_{13}H_{12}N_2O_2S$: C 59.98; H 4.64; N 10.76; S 12.32. Found: C 60.19; H 4.71; N 10.46; S 12.24%. FT-IR (cm^{-1}): υ(N—H) 3223 (m, br), 3161(w), 3118(w), υ(C—H) 3035(w), υ(C=O) 1663(vs), 1600(w), 1505(vs), 1449(m), 1323 (m), υ(C=S) 1259(s), 1166(s), 1107(m), 1084(w), 1070(m), 1019(s), 1000(w), 974(w), 918(m), 901(w), 884(m), 818(m), 791(m), 730(m), 688(s). ^1H NMR (*d*-acetone; δ, ppm): 11.18 (s, 1H, CSN*H*), 10.17 (s, 1H, CON*H*), 7.98 (d, *J* = 7.21 Hz, 2 H, Ph), 7.64 (t, *J* = 7.45 Hz, 1 H, Ph), 7.54 (d, *J* = 1.02 Hz, 1H, furane ring), 7.52 (t, *J* = 8.02 Hz, 2H, Ph), 6.45–6.41 (m, 2H, furane ring), 4.94 (d, *J* = 5.29 Hz, 2H, CH_2). ^{13}C NMR (*d*-acetone; δ, ppm): 207.3 (C=S), 182.4 (C=O), 169.4, 151.8, 144.3, 134.9, 133.9, 130.4, 129.8, 112.2, 110.0 (Ph and furane ring), 43.6 (CH_2).

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

Empirical formula	$C_{13}H_{12}N_2O_2S$
Formula weight	260.31
Temperature (K)	293.0
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.434(5)
b (Å)	11.822(5)
c (Å)	12.378(5)
α (°)	90.000(5)
β (°)	109.010(5)
γ (°)	90.000(5)
Volume (Å^3)	1305.2(10)
Z	4
ρ_{calc} (mg/mm^3)	1.325
m/mm^{-1}	0.243
F(000)	544.0
Crystal size/mm^3	0.078 × 0.095 × 0.208
2Θ range for data collection	6.9–61°
Index ranges	$-12 \leqslant h \leqslant 13$, $-11 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 16$
Reflections collected	6985
Independent reflections	3897[*R*(int) = 0.0535]
Data/restraints/parameters	3897/0/139
Goodness-of-fit on F^2	1.014
Final *R* indexes [$I \geqslant 2\sigma(I)$]	R_1 = 0.1040, wR_2 = 0.2686
Final *R* indexes [all data]	R_1 = 0.2413, wR_2 = 0.3939
Largest diff. peak/hole (e Å^{-3})	1.05/−0.48

Table 2
Selected bond lengths (Å), angels, torsion angles (Å) and interactions for **bftu**.

Bond length	XRD	Calc.	Bond angle	XRD	Calc.	Dihedral angle	XRD	Calc.
S1—C8	1.656(5)	1.676	C7—N1—C8	128.4(4)	129.27	N1—C7—C6—C5	−30.1(7)	−22.68
N1—C8	1.402(6)	1.405	C8—N2—C9	122.8(5)	122.68	N1—C7—C6—C1	150.3(5)	158.70
N1—C7	1.383(6)	1.382	N1—C8—S1	119.6(3)	118.35	O1—C7—C6—C5	150.7(5)	158.01
O1—C7	1.235(6)	1.226	N2—C8—S1	124.3(4)	125.51	O1—C7—C6—C1	−28.9(8)	−20.62
N2—C8	1.319(6)	1.336	N2—C8—N1	116.1(4)	116.15	C8—N1—C7—O1	−4.6(9)	−2.95
N2—C9	1.445(6)	1.464	N1—C7—C6	117.0(4)	115.71	C8—N1—C7—C6	176.3(4)	177.74
C7—C6	1.494(7)	1.497	O1—C7—N1	121.6(5)	122.58	C8—N2—C9—C10	−176.6(5)	−179.80
C6—C5	1.384(8)	1.401	O1—C7—C6	121.4(5)	121.71	C7—N1—C8—S1	−177.8(4)	−179.71
C6—C1	1.372(8)	1.400	C5—C6—C7	121.5(5)	119.34	C7—N1—C8—N2	1.4(7)	0.09
C10—C9	1.455(8)	1.487	C1—C6—C7	118.2(5)	117.17	C7—C6—C1—C2	−179.8(6)	179.90
C10—O2	1.336(8)	1.370	O2—C10—C9	120.6(6)	117.16	C10—O2—C13—C12	4.3(12)	−0.23
C10—C11	1.314(9)	1.361	C11—C10—C9	133.6(7)	133.17	C10—C11—C12—C13	−4.5(12)	−0.17
C5—C4	1.404(9)	1.392	C11—C10—O2	105.2(6)	109.66	C9—N2—C8—S1	−0.1(7)	−0.66
O2—C13	1.373(8)	1.363	N2—C9—C10	110.3(6)	111.50	C9—N2—C8—N1	−179.3(4)	179.56
C1—C2	1.367(8)	1.390	C6—C5—C4	119.4(6)	120.22	C9—C10—O2—C13	−179.0(8)	179.01
C4—C3	1.347(9)	1.394	C10—O2—C13	108.0(5)	107.21	C9—C10—C11—C12	177.5(9)	178.61
C2—C3	1.366(10)	1.395	C10—C11—C12	108.3(7)	106.64	O2—C10—C9—N2	107.3(9)	70.21
C11—C12	1.421(9)	1.434	C13—C12—C11	107.2(7)	106.08	C11—C10—C9—N2	−62.3(13)	−111.23
C12—C13	1.196(10)	1.358	C12—C13—O2	110.9(7)	110.41	C11—C10—O2—C13	−6.8(10)	0.12

Hydrogen bond geometries

D—H···A	d(D—H) (Å)	d(H—A) (Å)	d(D—A) (Å)	D-H-A/°
N1—H1—S1[1]	0.86	2.71	3.511(4)	155.5
N2—H2—O1	0.86	1.96	2.642(6)	135.8
C1—H1A—O1[2]	0.93	2.65	3.451(8)	145.4
C12—H12—O1[3]	0.93	2.54	3.460(8)	171.0

[1] $1-x, 2-y, 1-z$; [2] $1-x, 1-y, 1-z$; [3] $2-x, 1-y, 1-z$.

2.2. Antimicrobial studies

The newly prepared **bftu** were screened for their antibacterial activity against *Bacillus cereus* (ATCC 7064), *Entrococcus faecalis* (ATCC 29212), *Listeria monocytogenes* (ATCC 19114), *Streptococcus pneumoniae* (ATCC 29212), *Staphylococcus aureus* (ATCC 6538), *Methicillin Resistant Staphylococcus aureus MRSA* (ATCC 43300), and *Salmonella typhi* (CCM 5445), and *yeast. Candida albicans* (ATCC 10231) strains by the microdilution method. The antibacterial activity assays of all compounds were performed according to the Clinical and Laboratory Standards Institute (CLSI) protocols [50]. The antifungal activities of all compounds were evaluated according to the National Committee for Clinical Laboratory Standards (NCLS) [51]. All determinations were performed in triplicate and confirmed by three separate experiments. The MIC ($\mu g\ mL^{-1}$) was defined as the lowest concentration of compound inhibiting the growth of each strain. Vancomycine (Himedia) and Ciprofloxcacin (Sigma) for bacterial strains and Amphotericin B (Sigma) for fungal strains were used as a positive control.

3. Computational details

In the present work, we have used density functional theory (DFT/B3LYP) at the 6-311++G (d,p) basis set level for the computation of molecular structure and energies of the optimized structures. The entire calculations were performed by using Gaussian 09 [46] program package. Optimized structural parameter used by using vibrational wavenumbers and isotropic chemical shifts. The stability of the optimized structure was confirmed by frequency calculations, which give positive values. The total energy distribution (TED) was calculated by using VEDA 4 [47] program and the fundamental vibrational modes were characterized by their TED. For NMR calculations, after optimization, ^1H and ^{13}C NMR chemical shifts were calculated using the gauge-invariant atomic orbital (GIAO) method [48,49] in *d*-acetone solvent using IEF-PCM model. The chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra.

4. Results and discussion

1-Benzoyl-3-furan-2-ylmethyl-thiourea was prepared according to the method of Beyer and Widera [45]. The synthesis involves the reaction of a benzoyl chloride with ammonium thiocyanate in acetone followed by condensation of the benzoyl isothiocyanate with furfurylamine. There are two isomeric species of the compound; 1-(2-furoyl)-3-(o-tolyl)thiourea [52] and 1-furoyl-3-methyl-3-phenylthiourea [53]. These two compounds were synthesized from furoyl isothiocyanate. The compound was purified by re-crystallization from methanol and characterized by elemental analysis, ^1H, ^{13}C NMR, IR spectroscopy and single crystal X-ray diffraction analysis. The analytical and spectroscopic data are consistent with the proposed structure given in Fig. 1. Intermolecular interactions are also given in Fig. 2.

4.1. FT-IR spectrum

The experimental and theoretical Infrared spectra of **bftu** are shown in Fig. 3a and b, respectively, where calculated intensity is plotted against the wavenumbers. The observed and calculated wavenumbers along with their relative intensities and probable assignments with TED of title molecule are given in Table 3. The main vibrational bands of **bftu** are also given in the experimental section. Infrared spectra of these title compounds reveal all the expected frequency region of the υ(N—H), υ(C=O), υ(C=N) and υ(C=S).

It should be noted that the calculation was made for free molecule in vacuum, while the experiments were performed on the solid samples. Therefore, there are nonsignificant disagreements between them. The vibrational wavenumbers were crossed with a uniform scaling factor for agreement with experimental data well. The calculated wavenumbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and basis set deficiencies. Therefore, it is customary to scale down the calculated harmonic wavenumbers in order to improve the agreement with the experiment. In our

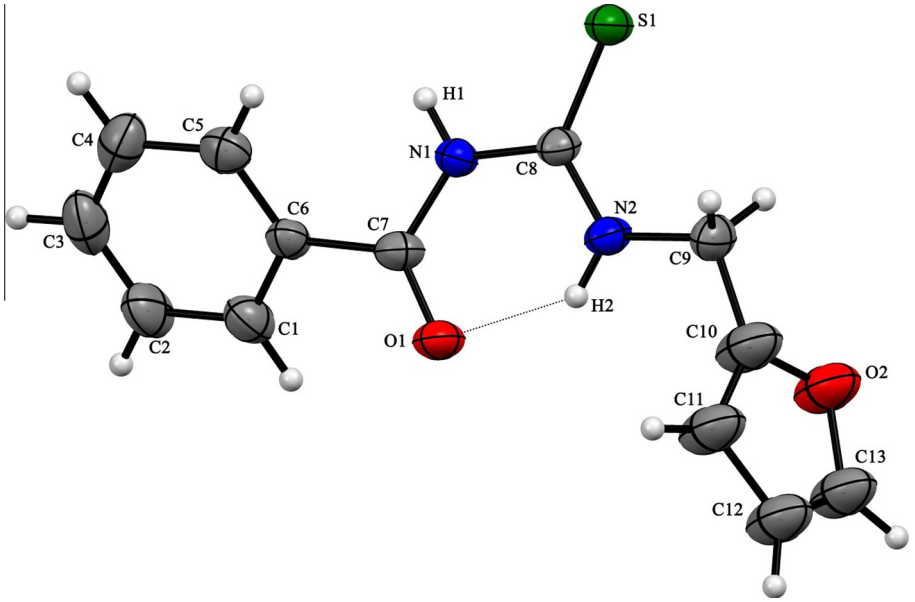

Fig. 1. The structure diagram with 50% probability ellipsoids of the compound (**bftu**) with atomic numbering scheme.

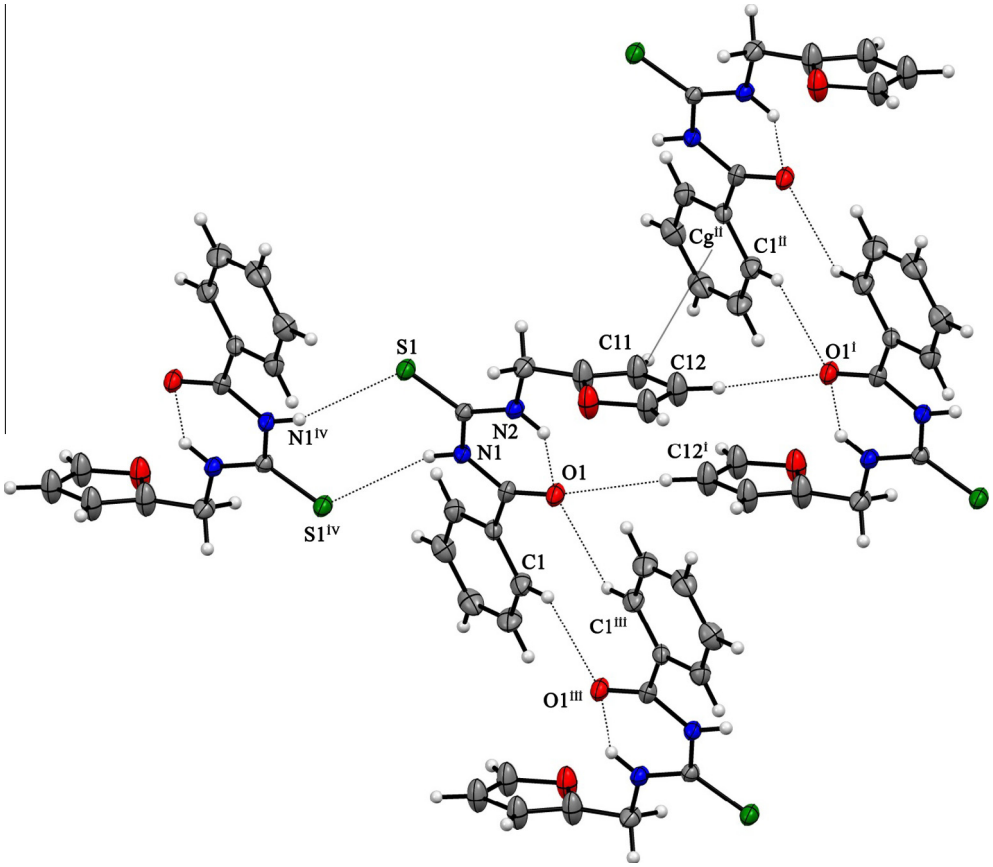

Fig. 2. Intermolecular interactions.

study, we have followed two different scaling factors, i.e. 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1} [54].

The bands at 3223 and 3161 cm^{-1} represent stretching vibration of N—H groups. The appropriate calculated frequencies of υNH are positioned at 3304 cm^{-1}, when DFTB3LYP/6-311++G(d,p) method was applied. The TED contribution of these stretching modes indicates that these are pure stretching modes. The intramolecular N_2—H···O=C hydrogen bond has a strong influence in the vibrational properties of the central —C(O)NHS(O)NH— moiety. These assignments were supported by the literature that υ(N1—H) can be seen at above 3200 cm^{-1} and the υ(N2—H) can be found at above 3000 cm^{-1} have been examined due to the

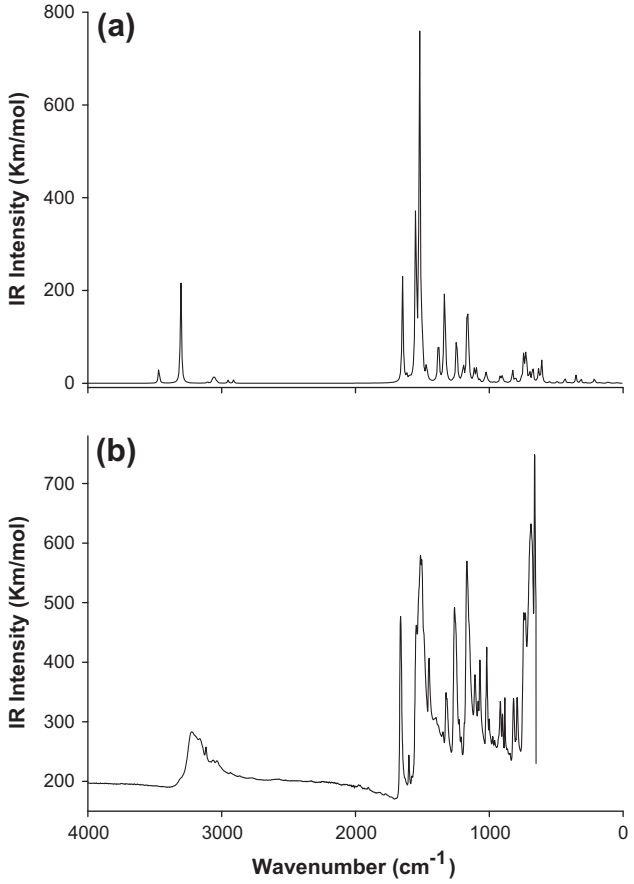

Fig. 3. (a) Theoretical and (b) experimental IR spectra of 1-benzoyl-3-furan-2-ylmethyl-thiourea (bftu).

existence of intramolecular hydrogen bonding [55–59,60]. The trans–cis conformation of **bftu** is related to the N—H stretching frequency range which are depends on the position —NHC(S)NHC(O)— group vibrations and stabilized by hydrogen bonding.

In aromatic compounds, the υCH, βCH and γCH vibrational modes are appeared in the range of 3000–3100, 1000–1300 and 750–1000 cm^{-1}, respectively [61,62]. In this study, towards the end the last ten vibrations are assigned to C—H stretching (3141–2909, modes 83–74), which correspond to stretching modes C—H of ring units. All modes are nearly pure stretching vibrations 100% TED terms. The υ(CH) stretching vibrations of the phenyl ring were assigned to a band observed at 3118 and 3035 cm^{-1}. The C—H in-plane bending vibrations appeared in the range 1496–1019 cm^{-1} (modes 66, 64–61, 56, 54, 53, 49 and 45) and their corresponding experimental wavenumbers, 1442–1019 cm^{-1} are in consistent with computed values. The assignments also find support from the literature [62–64].

The carbonyl stretching C=O vibration is expected to occur in the region 1715–1680 cm^{-1} [62,65]. The carbonyl band υ(C=O) of **bftu** is clearly observed at 1663 cm^{-1}which might be related to the resonance effect with the phenyl rings and existence of intramolecular hydrogen bonding with N—H [53–57,66]. The appropriate calculated frequencies are positioned at 1643 cm^{-1}.

The ring carbon–carbon stretching vibrations are appeared in the range of 1505–1600 cm^{-1}. The same vibration appears in the theoretical calculation at 1641, 1637, 1619 and 1505 cm^{-1}. The bands at 1000–1019 cm^{-1} should be attributed to the vibration of ring-breathing. The appropriate calculated frequencies are positioned at 1029 and 994 cm^{-1}. The band observed at 730 cm^{-1} in the FT-IR spectrum is assigned to C—C—C deformation of the phenyl ring. The same vibration appears in the theoretical calculation at 671 cm^{-1}.

It is well-known that both the amide and thiourea groups present a characteristic band in the 1500–1600 cm^{-1} range of the IR spectrum, originated by the N—H deformation δ mode [δ(N—H)] [31,67,68]. For the title compound, strong IR absorptions with defined maxima at ca. 1505 cm^{-1}.

The identification of other C—N vibration is a very difficult task, since the mixing of several bands is possible in this region. However, with the help of theoretical calculation (DFT), the C—N stretching vibrations are calculated. In the present investigation C—N stretching frequencies are observed at 1323, 1166, 1107 and 1010 cm^{-1} by FT-IR and their corresponding calculated wavenumbers appeared in the range of 1375–1065 cm^{-1}. These experimental values of C—N stretching mode show good agreement with theoretical values. The υCN stretching vibration normally appears around 1300 cm^{-1} [62,65].

The υ(NCN) bending vibration in thiourea is found around 500 cm^{-1}. The υ(NCS) bending vibration gives rise to a medium band at 626 cm^{-1} which is often difficult to identify. These are in fair agreement with that of the reported values [68–70].

Whilst, the υ(C=S) stretching vibration can be observed at 688–738 cm^{-1} range that are in close agreement with previously studied of other thiourea derivatives [59,71–73]. For instance, these vibrational modes show a good agreement with the 3-monosubstituted furoylthioureas series in the wide range at ca. 700 cm^{-1} [72]. The characteristic region of higher frequency υ(C=S) in the furoylthiourea derivatives is described as a large double bond character and the lower nucleophilic character of the sulfur atom in comparison with alkylthioureas. Comparing to this report, it can be concluded that the low frequency of the υ(C=S) in the spectrum of **bftu** has less double bond character between to the other similar compounds. Furthermore the low frequency values for the υ(C=S) stretching mode observed in the IR spectrum of the title compound can be related to the formation of intermolecular hydrogen bonds involving the thiocarbonyl group [31,74]. Indeed, C=S···H—N bonds are observed in the X-ray crystal structure of the compound, as will be discussed in the next section.

On the other hand, the vibrational frequencies in this range are influenced by probably due to the increased steric repulsion between the bulky sulfur atom and the hydrogen in furfurylamine and benzoyl in aromatic nuclei [59]. We have assigned two bands due to the C—S stretching based on the TED calculations, and obtained two bands at 800 and 795 cm^{-1} (mode 35) which the observed value are 791 and 688 cm^{-1}. In this study, four in-plane bending of S—C—N calculated at 543, 273, 206 and 171 cm^{-1} and four out-plane-bending of S—N—N—C calculated at 626–601 cm^{-1} based on TED calculation. The non-discussed modes details are given in Table 3. The majority of the theoretical FT-IR values show good agreement with experimental values.

4.2. NMR spectra

The ^{1}H NMR spectrum of **bftu** is consistent with the structural results. In ^{1}H NMR spectrum of **bftu**, one resonance can be observed at 4.94 ppm as doublet which are due to methylene protons of furfuryl group. The ^{1}H NMR spectrum shows doublet and triplets at 7.98–7.52 ppm for phenyl protons in **bftu**. Aromatic ring and furfuryl protons can be explained such as: the protons H1—H5, δ = 7.98 ppm (d, 2H, J = 7.21 Hz), appear in downfield. The proton H3 appears at δ = 7.64 ppm (t, 1H, J = 7.45 Hz), the protons H2 and H4 appear at δ = 7.52 ppm (t, 2H, J = 8.02 Hz), the proton H13 appears at 7.54 (d, 1H, J = 1.02 Hz), and the protons H11 and H12 appear at 6.45–6.41 ppm (m, 2H). The protons H9 appear at 4.94 ppm (d, 2H, J = 5.29 Hz). Two signals noted as singlet, corresponds to one

Table 3
Comparison of the theoretical and experimental vibrational spectra and proposal assignment[a].

	IR Exp.	IR Calc.	IR int.	TED (⩾10%)		IR Exp.	IR Calc.	IR int.	TED (⩾10%)
1		17	0.04	τCCNC(79)	43	1000	994	0.40	τHCCC,CCCC(85)
2		29	0.69	τCNCC,OCCN,CNCN(87)	44	1000	999	3.49	υCC(21) + βCCC(64)
3		38	0.40	τNCCC(61)	45	1019	1016	26.15	βHCC(57),COC(18)
4		42	0.75	βNCN,CCN,CNC(58)	46	1019	1029	10.18	υCC(41) + βCCC(11)
5		52	0.49	τCNCC,OCCN(60) + γ CCCC(10)	47	1070	1065	6.09	υNC(37)
6		94	1.60	βNCC,CCC(35) + τNCNC(22)	48	1084	1084	6.57	υOC(42) + βCCO(17)
7		108	2.98	τNCNC,NCCC(51)	49	1084	1092	28.05	υCC(28) + βHCC(32)
8		156	0.86	τCNCN(23) + γCCCC(21)	50	1107	1108	28.68	υNC(42) + βNCN,CNC(20)
9		171	1.35	βNCN,CNC,SCN(48) + τCOCC(10)	51	1166	1148	41.02	υOC(25) + βHCO(25)
10		206	11.04	βCNC,SCN(35) + τCNCN(15)	52	1166	1158	215.74	υNC(33))
11		222	1.91	τCNCC,CNCN(31)	53	1166	1166	3.75	υCC(10) + βHCC(73)
12		273	1.47	υNC,CC(22) + βCCC,SCN(41)	54	1166	1188	31.21	υCC(12) + βHCC(72)
13		308	10.83	βOCC(54) + τCOCC,OCCN(20)	55	1259	1198	11.82	υOC(16) + βHCN(26)
14		345	17.34	βOCN,CNC,OCC,CCC(58)	56	1259	1222	2.57	υOC,CC(27) + βHCC,HCO(40)
15		390	1.38	βOCN,CCN(31)	57	1259	1239	125.77	υCC(28) + βHNC(15)
16		404	0.59	τHCCC(24),CCCC(89)	58	1259	1263	4.22	βHCN(35) + τHCCC(29)
17		428	12.45	τCCCC(17) + γCCCC(16)	59	1323	1312	8.98	υCC(40)
18		486	4.63	βNCN,CCC(32)	60	1323	1328	222.59	υNC(10) + βHNC(10)
19		543	3.45	υCC(11) + βNCC,SCN(39)	61	1323	1334	34.98	βHCC(45)
20		601	23.95	τHNCN,CCOC(45) + γSNNC(33)	62	1323	1375	116.99	υNC(18) + βHCH(12) + τHCCC(11)
21		602	25.52	τHNCN,CCOC(56) + γSNNC(15)	63	1323	1389	1.80	βCCO,HCC,HCO(73)
22		619	5.70	βCCC(38) + τHNCN(14) + γSNNC(21)	64	1449	1452	3.10	βHCC(53)
23		626	26.53	τHNCN(40) + γSNNC(21)	65	1449	1464	34.70	βHCH(72) + τHCCC(14)
24		645	1.75	γCCOC(44)	66	1449	1496	80.91	βHCC(59)
25		666	20.76	βOCN,CCC(29) + τHNCN,CCCC(27)	67	1505	1505	42.56	υCC(56) + βHCO(16)
26		671	17.17	βCCC(10) + τHNCN(45)	68	1505	1517	803.90	βHNC(68)
27		692	23.58	τHCCC,CCCC(80)	69	1505	1545	427.74	υNC(37) + βHNC(45)
28	730	718	81.38	τHNCN(21) + γONCC(27)	70	1600	1591	8.07	υCC(44) + βCCC(10)
29	730	735	68.07	τHCCO(35),HCOC(89)	71	1600	1609	1.81	υCC(80)
30	730	752	8.63	υCC(12) + βCCO,COC(21)	72	1600	1613	11.19	υCC(39)
31	688	795	7.06	υSC(13) + γONCC(23)	73	1663	1643	227.55	υOC(76)
32	791	800	4.75	υSC(16) + τHCCC(11) + γONCC(16)	74	3035	2909	7.35	υCH(100)
33	818	820	30.95	τHCCC,HCCO,HCOC(63)	75	3035	2950	6.57	υCH(100)
34	818	844	1.05	τHCCC(98)	76	3035	3033	3.05	υCH(95)
35	884	869	1.61	τHCCC,HCCO,HCOC,CCOC(99)	77	3035	3039	2.34	υCH(98)
36	884	889	4.85	βCCO,COC(81)	78	3035	3050	13.11	υCH(85)
37	901	899	14.20	βOCN,CNC(33)	79	3035	3060	11.10	υCH(100)
38	918	913	14.00	υOC(23) + τHCCC(16)	80	3118	3070	4.95	υCH(97)
39	918	932	1.43	τHCCC(79)	81	3118	3106	3.09	υCH(94)
40	974	957	2.77	υCC(13) + τHCCC,OCCN(27)	82	3118	3116	0.08	υCH(99)
41	974	976	1.20	τHCCC(90)	83	3118	3141	0.09	υCH(98)
42	974	994	0.40	τHCCC,CCCC(85)	84	3161	3304	223.97	υNH(99)

[a] IRint – IR intensity (Kmmol-1), υ – stretching; β – in-plane-bending; γ-out-of-plane bending; τ – torsion. TED ⩾10% are shown.

proton at δ = 10.17 ppm which is assigned to the N1H1 proton which is substituted to the carbonyl and N2H2 proton and to the thione presence at δ = 11.18 ppm. In most compounds with aromatic substituents, the hydrogen bonded proton N2H2 has a higher δ ^{1}H value from acidic protons N1H1. These signals are different in term of chemical shift which is due to the intramolecular hydrogen bonded N—H bonds in the trans and cis conformations, respectively. As seen both NH signals are very close chemical shifts between δ 10–11 ppm due to deshielding aromatic ring [8,31,59].

In ^{13}C NMR spectrum, signals of the methylene carbon can be expected at above δ = 20 ppm. Meanwhile, the aromatic carbon resonances can be found in between δ = 129.8–144.3 ppm which is corresponding to the phenyl rings in the compound. The carbonyl and thione carbons can be clearly observed at δ = 207.3 and 182.4 ppm and more slightly deshielded in the spectra. Formation of intramolecular hydrogen bonding, the increasing electronegatively of oxygen and sulfur atoms and different environment and conformations cause a deshielding effect for these signals [8,59,71].

The results of theoretical NMR calculation are also given in Table 4. The molecular structure of title compound was optimized before theoretical NMR calculation. Then, gauge-including atomic orbital (GIAO) [40,41] ^{13}C NMR and ^{1}H NMR chemical shift calculations were carried out by using B3LYP functional with 6-311++G(d,p) basis sets. The isotropic shielding values were used to calculate the isotropic chemical shifts with respect to tetramethylsilane (TMS). As seen from Table 4, experimental and theoretical results are in perfect agreement. The biggest differences between theoretical and experimental values are 17.67 ppm (8.5%) for C8 and 1.2 ppm (11.8%) for N1H1, respectively.

4.3. Description of the crystal structure

The structure of 1-benzoyl-3-furan-2-ylmethyl-thiourea was confirmed by the result of a single crystal X-ray structure determination. Fig. 1 shows the molecular structure of **bftu**. Experimental details for data collection and structure refinement are summarized in Table 1. The selected bond lengths and angles are presented in Table 2 (includes intra and intermolecular interactions). Both of the C8—S1 (1.656(5) Å) and C7—O1 (1.235(6) Å) bonds show typical double-bond characteristics [26,52,53,56,59,75]. However, the C—N bond lengths C7—N1 (1.383(6) Å), C8—N1 (1.402(6) Å) and C8—N2 (1.319(6) Å) are shorter than the normal C—N single-bond length of about 1.48 Å [26,52,53,56,59,75]. The shortening of these C—N bonds reveals the effects of resonance in this part of the molecule. The N1—C8 = 1.402(6) Å and N2—C8 = 1.319(6) Å bond length differ significantly from each other. The N2—C8 bond length is shorter than N1—C8 bond length. This may be due to the strong intramolecular hydrogen [O···H—N] bonding between the keto (C=O) group

Table 4
The experimental and predicted ^{13}C and ^{1}H isotropic chemical shifts (with respect to TMS, all values in ppm) for 1-benzoyl-3-furan-2-ylmethyl-thiourea.

Atom	Exp.	B3LYP	Atom	Exp.	B3LYP
C8	207.31	189.64	N2H2	11.18	10.47
C7	182.38	173.07	N1H1	10.17	8.97
C10	169.42	158.08	H1	7.98	8.22
C13	151.85	151.56	H5	7.98	8.22
C3	144.34	141.00	H3	7.64	7.93
C6	134.86	139.33	H4	7.52	7.86
C1	133.91	136.69	H2	7.52	7.86
C2	130.36	135.78	H13	7.54	7.80
C4	130.36	135.78	H11	6.45–6.41	6.78
C5	129.80	132.43	H12	6.45–6.41	6.68
C11	112.22	118.61	H9a	4.94	4.76
C12	109.98	116.99	H9b	4.94	4.76
C9	43.57	47.207			

and the amine (—NH—) nitrogen. The bond C8—S1 = 1.656(5) Å is significantly longer than a double C—S bond of 1.56 Å but smaller than single C—S bond distance of 1.82 Å [8,68–70]. Consequently, the C—S bond like in these compounds possesses only partial double-bond character. All other bond lengths fall within the expected ranges for in the N-alkyl-N′-benzoylthiourea compounds [26,52,53,56,59,75].

These results are in agreement with the expected delocalization in **bftu** and confirmed by C7—N1—C8 = 128.4(4)° and C8—N2—C9 = 122.8(5)° showing sp^2 hybridization on N1 and N2. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles C8—N1—C7—O1, C7—N1—C8—N2 and C7—N1—C8—S1 −4.6(9), 1.4(7) and −177.8(4), respectively.

The phenyl and furan rings are nearly planar and the angle between the two ring planes is found as 77.9(4)°. The C12 atom of the furan ring formed a hydrogen bond with the O1 atom of the molecule at $2-x, 1-y, 1-y$. The C11 atom of the furan ring showed C—H···π interactions with the phenyl ring center at $1+x, y, z$. The C1 atom of phenyl ring acts as hydrogen bond donor via its hydrogen atom to the O1 atom of the molecule at $1-x, 1-y, 1-z$. In addition to these interactions, another hydrogen bond was detected between the N1 atom thiourea part and sulfur atom of thiourea part at $1-x, 2-y, 1-z$. So, these interactions expand the molecules through the three axes to form a three dimensional network in the solid state.

The structural parameters are also calculated as theoretically. The optimized bond lengths, bond angles, and selected dihedral angles of compound calculated with B3LYP method and 6-311++G(d,p) basis set are listed in Table 2. From the table it is seen that the various bond lengths are found to be greater than experiment for the title molecule. This overestimation can be explained that theoretical calculations belong to isolated molecule in the gaseous phase and the experimental results belong to similar molecule in the solid state. Especially, the theoretical bond lengths between carbon atoms are generally greater than experiment. Additionally, the theoretical S—C bond length is greater. We couldn't say it for N—C or O—C bond distances. The bond lengths are well correlated by cross 0.9873 with observed data. Arslan et al. [75] reported that DFT method correlates ($r = 0.9952$) well for the bond length compared with the HF method.

4.4. Hyperpolarizability

The first hyperpolarizability (β_0) and related properties (β, α_0 and $\Delta\alpha$) of **bftu**, are calculated using B3LYP/6-311++G(d,p) basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyper polarizability is a third rank tensor that can be described by a $3\times3\times3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [76,77]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3\times3\times3$ matrices is a tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, the expansion becomes:

$$E = E_0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + \cdots \quad (1)$$

where E_0 is the energy of the unperturbed molecules, F_α the field at the origin $\mu_\alpha, \alpha_{\alpha,\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyper polarizabilities, respectively. The total static dipole moment μ, the mean polarizability α_0, the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyper polarizability β_0, using the x, y, z components are defined as:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}} \quad (2)$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (3)$$

$$\Delta\alpha = 2^{-1/2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2\right]^{1/2} \quad (4)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \quad (5)$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xxy} \quad (6)$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \quad (7)$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \quad (8)$$

Since the values of the polarizabilities (α) and hyperpolarizability (β) of the Gaussian 09 output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) (α: 1 a.u. = 0.1482×10^{-24} esu; β: 1 a.u. = 8.639×10^{-33} esu) and given in Table 5 for **bftu**.

It is well known that the higher values of dipole moment, molecular polarizability, and hyper polarizability are important for more active nonlinear optical (NLO) properties. The calculated dipole moment is equal to 1.3926 Debye (D). The highest value of dipole moment is observed for component μ_y. In this direction this value is equal to 1.0825 D. The calculated polarizability α_{ij} have non-zero values and was dominated by the diagonal components. The total polarizability (α_{tot}) and anisotrophy of polarizability ($\Delta\alpha$) were calculated as 30.0830 esu and 17.1312 esu. The magnitude of hyper polarizability β, is one of important key factors in a NLO system. The total first hyper polarizability value β_{tot} is equal to 3.5462×10^{-30} esu. The hyper polarizability β dominated by the longitudinal components of β_{xxx}. Domination of particular component indicates on substantial delocalization of charges in this direction.

The μ and β values of urea are reported as 1.528517 Debye and 343.272×10^{-33} esu in Ref. [78] by HF/6-311G (d,p) method. Total dipole moment of studied molecule is approximately equal to those of urea. The first hyper polarizability component of title molecule 10 times greater than urea. That is to say, the title molecule can be a good candidate of NLO materials.

4.5. Antimicrobial activities

Bftu showed different degrees of antimicrobial activity in relation to the tested species. **Bftu** showed inhibition against at *L.*

Table 5
The electric dipole moment (Debye), Polarizability and first hyper polarizability of bftu.

	a.u.	esu. ($\times 10^{-24}$)		a.u.	esu. ($\times 10^{-33}$)
α_{xx}	258.7489	38.3466	β_{xxx}	448.2514	3872.4438
α_{xy}	−1.2401	−0.1838	β_{xxy}	239.5934	2069.8474
α_{yy}	221.1765	32.7784	β_{xyy}	−281.4110	−2431.1096
α_{xz}	4.0525	0.6006	β_{yyy}	−250.9000	−2167.5216
α_{yz}	7.2276	1.0711	β_{xxz}	−26.2901	−227.1202
α_{zz}	129.0416	19.1240	β_{xyz}	51.5532	445.3681
α_{tot}	202.9890	30.0830	β_{yyz}	40.8101	352.5585
$\Delta\alpha$	115.5952	17.1312	β_{xzz}	5.1388	44.3941
μ_x	−0.8138		β_{yzz}	67.3402	581.7520
μ_y	−1.0825		β_{zzz}	−1.5203	−13.1339
μ_z	0.3243		β_{tot}	410.4841	3546.1725
μ	1.392569				

monocytogenes, B. cereus and *S. aureus* 256 μg mL^{-1} concentration. **Bftu** showed no activity the other microorganisms. The biological activities of 1-(benzoyl)-3-(substituted) thioureas have generally low antibacterial activity. If they have aromatic rings included halogens (Cl, Br, etc.) their antimicrobial activities increase [79–81]. The same result was seen in bftu.

5. Conclusions

The new thiourea derivative, 1-benzoyl-3-furan-2-ylmethyl-thiourea was synthesized and several properties were studied using FT-IR, ^{13}C, ^{1}H NMR spectroscopy and tools derived from the density functional theory. The single crystal X-ray diffraction data and calculated geometrical parameters compared. For agreement between them, we found the scaling factor value of 0.9873 for DFT/6-311++G(d,p). At the frequency and NMR calculations used the B3LYP method with the standard 6-311++G(d,p) basis sets. The small difference between experimental and calculated geometrical parameters and vibration mode can come from the difference of the state. In general, it is seen acceptable general agreement between experimental and theoretical data which indicates that the theoretically optimized geometry of the **bftu** molecule closely matches with the crystal data of the observed molecule. The theoretical calculations showed that the title compound can be a good candidate of NLO materials. **Bftu** exhibited antimicrobial activity against, *L. Monocytogenes, B. cereus* and *S. aureus*.

Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 891971. A copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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