FT-IR, FT-Raman and UV-Visible Spectral Analysis on (E)-N′-(thiophen-2-ylmethylene) Nicotinohydrazide

Abstract
Vibrational analysis of the (E)-N′-(thiophen-2-ylmethylene) nicotinohydrazide (T2CNH) compound was carried out in solid phase using FTIR and FT-Raman spectroscopic techniques in the ranges: 400-4000 cm\(^{-1}\) and 100-4000 cm\(^{-1}\), respectively. The molecular geometries and harmonic vibrational frequencies were calculated using DFT/6-311++G(d,p) basis set. A detailed interpretation of the IR and Raman spectra, based on the total energy distribution (TED) of the normal modes. The bond parameters such as bond lengths, bond angles and dihedral angles were calculated at the same level of theory. The natural bonding orbital (NBO) study reveals that inter and intra-molecular charge transfer of the molecule. The electronic transition was studied using UV-Vis spectrum. The NLO, band gap energy, MEP map, Mulliken atomic charges were calculated using the same level of basis set. In addition the thermodynamic properties were also calculated.

Keywords: FT-IR; FT-Raman; TED; NBO; T2CNH

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Received: December 21, 2016; Accepted: January 02, 2017; Published: January 09, 2017

Introduction
Generally, Pyridine ring is a heterocyclic organic compound with the chemical formula C\(_5\)H\(_5\)N. Pyridine is structurally related to benzene, with one methine group (=CH-) replaced by a nitrogen atom. It occurs in many important compounds, including azines and the vitamins niacin and pyridoxal. The precursor of pyridine is used to agrochemicals, pharmaceuticals and is also an important solvent and reagent. Mostly, it is used in the in vitro synthesis of DNA, sulfa pyridine (a drug against bacterial and viral infections), antihistaminic drugs triphenylenamine and mepyramine, as well as water repellents, bactericides, and herbicides. Some chemical compounds, although not synthesized from pyridine, contain its ring structure. They include B vitamins niacin and pyridoxal, an anti-tuberculosis drug isoniazide, nicotine and other nitrogen-containing plant products [1].

The ring of Thiophene and its derivatives have been reported to possess broad spectrum of biological properties including anti-inflammatory, analgesic, antidepressant, antimicrobial and anticonvulsant activities [2-4]. Antiepileptic drugs (AEDs) like tiagabine, etizolam, brotizolam are containing thiophene moiety in their structures as active pharmacophore [5,6]. In addition, thiophene and its derivatives functionalized with the formyl group are versatile building blocks for the synthesis of donor-acceptor substituted p-conjugated systems for several optical applications.

The hydrazone group in the organic compound brings out several physical and chemical properties. The hydrazones are bearing the \(\text{C} = \text{N}-\text{N}\) which leads the molecule towards nucleophilic and electrophilic in nature. In the hydrazone moiety, the nitrogen atom behaves as nucleophilic and carbon atom behaves as nucleophilic as well as electrophilic in nature [7-9]. The benzohydrazide derivatives shows wide spectrum of...
biological activities such as antibacterial [10], antifungal [11] and antitubercular [12] activities.

Subashchandrabose et al. [13] recorded the FT-IR, FT-Raman and UV-Vis spectra for the molecule N1-N2-bis((pyridine-4-1) methylene)benzene-1,2-diamine. The observed FT-IR and FT-Raman spectral values were compared with the calculated wavenumbers. For the prediction of accurate vibrational assignments TED analysis was performed using SQM method. The bond lengths and bond angles of stable conformer were correlated well with the experimental values. The hyperconjugative interaction and charge delocalization around the bonds were studied using NBO analysis. Band gap energy was also determined.

Quantum chemical calculations of energies, geometrical structure and vibrational wavenumber of 1,2-bis(3-methoxy-4-hydroxybenzylidene)hydrazine were carried out by Subramanian et al. [14] using DFT method with 6-31G(d) as basis set. The optimized geometrical parameters obtained by DFT calculations are in good agreement with single crystal XRD data. The vibrational spectral data were obtained from FT-IR and FT-Raman spectra are assigned based on the results of the theoretical calculations in solid phase.

From Literature survey reveals that the vibrational analysis of (E)-N′-(thiophen-2-ylmethylene) nicotinohydrazide (T2CNH) has not yet been reported. The T2CNH molecule was synthesized and its structural characterization was calculated by B3LYP/6-311++G(d,p) basis set. The spectral investigation such as FT-IR, FT-Raman and UV-Vis spectra were recorded. The observed spectral results were compared with the computed wavenumber. The vibrational assignments of the title molecule were carried out with the help of TED. The First order hyperpolarizability, Homolumo energy gap was calculated and furthermore, the MEP and vibrational wavenumbers using DFT/B3LYP/6-311++G(d,p) basis set. The spectral data were obtained from FT-IR and FT-Raman spectra are out-of-plane bending vibrations and all of them are IR and Raman active [25]. The calculated and observed vibrational wavenumbers using DFT/B3LYP/6-311++G(d,p) basis set, along with their relative intensities are given in Table 2. The total energy distribution (TED) was calculated using SQM program [26]. The

**Experimental Details**

**Synthesis procedure**

A mixture of Thiophene-2-carboxaldehyde (2.1 ml, 0.01 mol) and nicotinic acid hydrazide (1.37 g, 0.01 mol) in 5 mL of ethanol was stirred in the presence of 2 drops of concentrated HCl for one hour. The reaction mixture was maintained at room temperature and the colourless solid was obtained. The solid was separated and filtered under suction, washed with ice-cold water (50 ml). The precipitate was washed with water and filtered and again washed with petroleum ether (40-60%) and dried over in a vacuum desicator then the product was recrystallized from hot ethanol.

![Synthesis procedure](http://www.imedpub.com/archives-in-chemical-research/)

**Results and Discussion**

**Molecular Geometry**

The T2CNH molecule was optimized by B3LYP/6-311++G(d,p) level of basis set. This molecule consists of thiophene and pyridine rings are fused by hydrazone linkage. The calculated bond length of C2-S1 bond length, since the hydrazono moiety is attached with C2 atom and their corresponding bond distances are 1.750 and 1.728 Å. The bond lengths of C=S-Cy, C=C-Cy, C=S-Cy, C=S-Cy, C=C-Cy are 1.377, 1.418, 1.369 Å and the bond angles of C2-C3-C4, C3-C4-C5 are 113.02°, 113.03°. The bond angles S1-C2-C3 and S1-C2-C4 differ by ~1° which is due to the shortening of bond distance between S1 and C2 atoms. These values are particularly in good agreement with the values of anti thiophen-2-aldehyde [20] and thiophen-2-carboxyhydrazide [21]. Furthermore, these values are also find support from literature [22]. The dihedral angles of S1-C2-C3-N1/ S1-C2-C3-H10 and C2-C3-C4-N1/C2-C3-H10 are -179.96°/-0.07° and 0.03°/+179.93°, respectively, which shows that the thiophen and hydrazono moieties of T2CNH are co-planar. Since there is a good conjugation between p-orbitals of all atoms of thiophen and hydrazono moieties. Most of the calculated geometrical parameters are find support from single crystal X-ray diffraction values [23,24]. It should be mentioned that there is no significant difference between the geometrical parameters of the hydrazono and pyridine moieties [23,24]. The geometrical parameters and optimized structure of the T2CNH molecule are presented in Table 1 and Figure 1, respectively.

**Vibrational Assignments**

The T2CNH molecule belongs to C1 point group symmetry. It consists of 25 atoms which undergoes 69 normal modes of vibrations. In which 47 modes of vibrations are in-plane and 22 are out-of-plane bending vibrations and all of them are IR and Raman active [25]. The calculated and observed vibrational wavenumbers using DFT/B3LYP/6-311++G(d,p) basis set, along with their relative intensities are given in Table 2. The total energy distribution (TED) was calculated using SQM program [26]. The

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**Table 1**

| Mode | Description | IR Wavenumber (cm⁻¹) | Raman Wavenumber (cm⁻¹) |
|------|-------------|----------------------|------------------------|
| 1    | in-plane    | 1500                 | 1400                   |
| 2    | out-plane   | 2500                 | 2600                   |
| 3    | in-plane    | 3000                 | 3100                   |
| 4    | out-plane   | 4000                 | 4100                   |

**Table 2**

| Mode | Description | IR Wavenumber (cm⁻¹) | Raman Wavenumber (cm⁻¹) |
|------|-------------|----------------------|------------------------|
| 1    | in-plane    | 1500                 | 1400                   |
| 2    | out-plane   | 2500                 | 2600                   |
| 3    | in-plane    | 3000                 | 3100                   |
| 4    | out-plane   | 4000                 | 4100                   |

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![Vibrational Assignments](http://www.imedpub.com/archives-in-chemical-research/)
Table 1: The optimized bond parameters of T$_2$CNH.

| Bond Parameters | B3LYP/6-311++G(d,p) | XRD $^{a,b,c}$ |
|-----------------|---------------------|----------------|
| Bond Lengths (Å) |                     |                |
| S1-C2           | 1.750               | 1.728$^b$      |
| S1-C5           | 1.728               | 1.717$^a$, 1.707$^b$ |
| C2-C3           | 1.377               | 1.375$^a$, 1.362$^b$ |
| C2-C9           | 1.448               |                |
| C3-C4           | 1.418               | 1.431$^a$, 1.392$^b$ |
| C3-H8           | 1.081               | 1.114$^a$      |
| C4-C5           | 1.369               | 1.345$^a$      |
| C9-H10          | 1.097               | 0.930$^a$      |
| C9-N11          | 1.282               | 1.266$^a$      |
| N11-N12         | 1.357               | 1.375$^a$      |
| N12-H13         | 1.016               | 0.860$^a$      |
| N12-C14         | 1.385               | 1.354$^a$      |
| C14-O15         | 1.213               | 1.224$^a$      |
| C16-C17         | 1.399               | 1.384$^a$      |
| C16-C18         | 1.397               | 1.371$^a$      |
| C17-N19         | 1.335               | 1.334$^a$      |
| C17-H20         | 1.087               | 0.930$^a$      |
| C18-C21         | 1.387               | 1.368$^a$      |
| C18-H22         | 1.083               | 0.930$^a$      |
| N19-C23         | 1.335               | 1.337$^a$      |
| C21-C23         | 1.395               | 1.368$^a$      |
| C23-H25         | 1.086               | 0.930$^a$      |
| Bond Angles (°) |                     |                |
| C2-S1-C5        | 91.57               | 92.00$^a$, 91.81$^b$ |
| S1-C2-C3        | 110.68              | 111.80$^a$     |
| C2-C3-C4        | 112.02              | 112.20$^a$, 114.72$^b$ |
| C2-C3-H8        | 122.16              | 129.20$^a$     |
| C3-C4-C5        | 113.03              | 112.05$^a$     |
| S1-C5-C4        | 111.68              | 112.13$^a$     |
| N12-C14-C16     | 114.21              | 114.95$^a$     |
| O15-C14-C16     | 122.13              | 121.48$^a$     |
| C16-C17-N19     | 123.88              | 122.05$^a$     |
| C16-C17-H20     | 120.91              | 120.03$^a$     |
| N19-C17-H20     | 115.16              | 118.20$^a$     |
| C16-C18-C21     | 118.94              | 118.91$^a$     |
| C16-C18-H22     | 119.08              | 120.50$^a$     |
| C21-C18-H22     | 121.96              | 120.30$^a$     |
| C17-N19-C23     | 117.47              | 117.44$^a$     |
| C18-C21-C23     | 118.58              | 118.58$^a$     |
| C18-C21-H24     | 121.13              | 120.71$^a$     |
| C23-C21-H24     | 120.27              | 120.70$^a$     |
| N19-C23-C21     | 123.40              | 123.64$^a$     |
| Dihedral Angles (°) |                 |                |
| S1-C2-C9-H10    | -0.07               |                |
| S1-C2-C9-N11    | -179.96             |                |
| C3-C2-C9-H10    | 179.93              |                |
| C3-C2-C9-N11    | 0.03                |                |
| C2-C3-C4-C5     | 0.02                |                |
| C2-C3-C4-H7     | -179.98             |                |
| H8-C3-C4-C5     | 179.97              |                |
| H8-C3-C4-H7     | -0.03               |                |
| C3-C4-C5-S1     | -0.01               |                |
| C3-C4-C5-H6     | -179.99             |                |

$^a$Brathen O, Kveseth KJ, Hagen K (1986) J Mol Struct 145: 45.
$^b$Geiger DK, Geiger HC, Williams L, Noll BC (2012) Acta Cryst E 68 : 0420.
$^c$Ramesh Babu N (2014) J Mol Struct 1072: 84-93.

combined vibrational spectra of T2CNH molecule are shown in Figures 2 and 3.

N-H vibrations

The N-H stretching vibration appears in the region of 3300-3500 cm$^{-1}$ [27]. In accordance with the above literature the νN-H vibration has been observed at 3401 cm$^{-1}$ in FTIR spectrum, whereas the harmonic wavenumber assigned at 3365 cm$^{-1}$ (mode no: 1) and its TED value is 100% it should be noted here that, a small deviation between theoretical and experimental value is only due to intra-molecular charge transfer between amino and carbonyl group in hydrazone linkage. The harmonic wavenumbers (1508/ mode no: 14 and 488 cm$^{-1}$/mode no: 53) of βN-H and γN-H modes were presented in Table 2 are found to be in good agreement with literature [28] data 1476 and 535 cm$^{-1}$ as well as with the structurally related molecule. Mode no: 14 is in agreement with observed FT-Raman band at 1519 cm$^{-1}$ and these assignments also find support from TED values (22% and 61%).

C-H vibrations

In aromatic compounds, the νCH,  βCH and γCH vibrations are expected to appear in the ranges of 3100-3000 cm$^{-1}$, 1400-1000 cm$^{-1}$ and 1000-750 cm$^{-1}$ respectively [29,30]. In this study, the aromatic C-H stretching vibration is observed at 3059 cm$^{-1}$/FT-IR, whereas the calculated wavenumbers are in the range 3076-3016 cm$^{-1}$ (mode nos. 5 and 9). The in-plane C-H bending vibrations are assigned at 1425, 1290 cm$^{-1}$ in FT-IR and 1429, 1300 & 1195 cm$^{-1}$ in FT-Raman spectra and their corresponding calculated wavenumbers are 1447, 1391, 1308, 1173 cm$^{-1}$ (mode nos: 16, 18, 21, 25). The harmonic wavenumbers occur in the region of 974-808 cm$^{-1}$ (mode nos: 34-36, 42) are assigned to C-H out-of-plane bending modes, in which mode no: 35 is in agreement with observed wavenumber values: 955 cm$^{-1}$ (FT-Raman) and 948 cm$^{-1}$ (FT-IR). These assignments are in line with literature values [14] and also find support from TED Values.
Figure 1  The Optimized structure of (E)-N’-(thiophen-2-ylmethylene) nicotinohydrazide (T2CNH).

| Mode No | Calculated Frequencies (cm⁻¹) | Observed Frequencies cm⁻¹ | IR Intensity | Raman Intensity | Reduced Masses | Force Constants | Vibrational assignments≥10% (TED) |
|---------|-----------------------------|--------------------------|--------------|----------------|----------------|----------------|---------------------------------|
|         | UnScaled | Scaled | FT-IR | FT-Raman | Abs. | Rel. | Abs. | Rel. | | |
| 1       | 3503    | 3365   | 3401  w | 3365  w | 134.41 | 1.67 | 1.08 | 7.78 | vN$_{H_2}$ (100) |
| 2       | 3247    | 3120   | 3171  w | 3120  w | 101.27 | 1.26 | 1.10 | 6.82 | vC$_H$ (94) |
| 3       | 3223    | 3096   | 3096  w | 3062  w | 34.50  | 0.57 | 0.16 | 7.42 | vC$_H$ (97) |
| 4       | 3204    | 3078   | 3079  w | 3059  w | 72.48  | 7.00 | 1.94 | 6.29 | vC$_{18H_22}$ (99) |
| 5       | 3202    | 3076   | 3076  w | 3059  w | 72.48  | 7.00 | 1.94 | 6.29 | vC$_{18H_22}$ (99) |
| 6       | 3187    | 3062   | 3059  w | 3059  w | 84.20  | 9.14 | 2.54 | 6.14 | vC$_{21H_24}$ (95) |
| 7       | 3156    | 3032   | 3027  w | 3027  w | 72.48  | 9.14 | 2.54 | 6.14 | vC$_{21H_24}$ (95) |
| 8       | 3139    | 3016   | 3016  w | 3016  w | 72.48  | 9.14 | 2.54 | 6.14 | vC$_{21H_24}$ (95) |
| 9       | 3019    | 2901   | 2901  w | 2901  w | 72.48  | 9.14 | 2.54 | 6.14 | vC$_{21H_24}$ (95) |
| 10      | 1757    | 1688   | 1673  s | 1673  s | 1670  w | 1670  w | 1670  w | 1670  w | vO$_{C_1}$ (85) |
| 11      | 1656    | 1591   | 1592  s | 1592  s | 1591  w | 1591  w | 1591  w | 1591  w | vC$_{12H_13}$(100) |
| 12      | 1627    | 1563   | 1563  s | 1563  s | 1563  s | 1563  s | 1563  s | 1563  s | vC$_{12H_13}$(100) |
| 13      | 1605    | 1542   | 1542  s | 1542  s | 1542  s | 1542  s | 1542  s | 1542  s | vC$_{12H_13}$(100) |
| 14      | 1570    | 1508   | 1508  s | 1508  s | 1508  s | 1508  s | 1508  s | 1508  s | vC$_{12H_13}$(100) |
| 15      | 1551    | 1490   | 1490  s | 1490  s | 1490  s | 1490  s | 1490  s | 1490  s | vC$_{12H_13}$(100) |
| 16      | 1506    | 1447   | 1425  m | 1425  m | 1425  m | 1425  m | 1425  m | 1425  m | vC$_{12H_13}$(100) |
| 17      | 1459    | 1402   | 1402  m | 1402  m | 1402  m | 1402  m | 1402  m | 1402  m | vC$_{12H_13}$(100) |
| 18      | 1448    | 1391   | 1391  m | 1391  m | 1391  m | 1391  m | 1391  m | 1391  m | vC$_{12H_13}$(100) |
| 19      | 1390    | 1335   | 1335  m | 1335  m | 1335  m | 1335  m | 1335  m | 1335  m | vC$_{12H_13}$(100) |
| 20      | 1387    | 1333   | 1333  m | 1333  m | 1333  m | 1333  m | 1333  m | 1333  m | vC$_{12H_13}$(100) |
| 21      | 1362    | 1308   | 1290  s | 1290  s | 1290  s | 1290  s | 1290  s | 1290  s | vC$_{12H_13}$(100) |
| 22      | 1291    | 1240   | 1240  s | 1240  s | 1240  s | 1240  s | 1240  s | 1240  s | vC$_{12H_13}$(100) |
| 23      | 1268    | 1219   | 1218  m | 1218  m | 1218  m | 1218  m | 1218  m | 1218  m | vC$_{12H_13}$(100) |
| 24      | 1265    | 1215   | 1215  s | 1215  s | 1215  s | 1215  s | 1215  s | 1215  s | vC$_{12H_13}$(100) |
| 25      | 1221    | 1173   | 1173  m | 1173  m | 1173  m | 1173  m | 1173  m | 1173  m | vC$_{12H_13}$(100) |
| 26      | 1195    | 1148   | 1145  m | 1145  m | 1145  m | 1145  m | 1145  m | 1145  m | vC$_{12H_13}$(100) |
| 27      | 1142    | 1097   | 1097  s | 1097  s | 1097  s | 1097  s | 1097  s | 1097  s | vC$_{12H_13}$(100) |
| 28      | 1134    | 1090   | 1090  s | 1090  s | 1090  s | 1090  s | 1090  s | 1090  s | vC$_{12H_13}$(100) |
| 29      | 1102    | 1059   | 1059  s | 1059  s | 1059  s | 1059  s | 1059  s | 1059  s | vC$_{12H_13}$(100) |
| 30      | 1086    | 1044   | 1044  s | 1044  s | 1044  s | 1044  s | 1044  s | 1044  s | vC$_{12H_13}$(100) |
| 31      | 1058    | 1017   | 1031  w | 1031  w | 1031  w | 1031  w | 1031  w | 1031  w | vC$_{12H_13}$(100) |
| No. | 32   | 33   | 34   | 35   | 36   | 37   | 38   | 39   | 40   | 41   | 42   | 43   | 44   | 45   | 46   | 47   | 48   | 49   | 50   | 51   | 52   | 53   | 54   | 55   | 56   | 57   | 58   | 59   | 60   | 61   | 62   | 63   | 64   | 65   | 66   | 67   | 68   | 69   |
|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1056| 1015 | 7.59 | 2.11 | 414.19 | 5.14 | 1.76 | 1.15 | $\beta H C C_2(14)+\beta H C C_2(27)+\nu C C(35)$ | $\beta C C_2 N_2 C_2(32)+\beta C C_2 N_2(15)+\beta C C_2 N_2(25)$ | $\tau C C_2 C_2(75)+\tau C C_2 N_2 H_2(18)$ | $\Gamma C_2 C_2 N_2 H_2(50)+\tau C C_2 C_2 N_2 H_2(12)+\tau C C_2 C_2 N_2 H_2(30)$ | $\Gamma C C_2 N_2 H_2(71)$ | $\Gamma C C_2 N_2 H_2(80)$ | $\nu H C C_2(46)+\tau C C_2 N_2 H_2(32)$ | $\beta N_2 C_2 O_2(20)+\beta C N_2 N_2(25)$ | $\nu C C_2(10)+\beta C C_2 N_2(20)+\nu S C C_2(17)$ | $\beta C S C_2(80)$ | $\beta C S C_2 C_2 H_4(36)+\tau C C_2 C_2(55)$ | $\beta C C_2 N_2(17)+\tau C C_2 N_2 C_2(16)+\tau C C_2 N_2 C_2(16)+\tau C C_2 N_2 C_2(10)$ | $\tau C C_2 N_2 C_2(27)+\tau C C_2 N_2 C_2(22)+\tau C C_2 N_2 C_2(16)$ | $\nu C C_2(22)+\tau S C C_2 C_2(22)+\tau C C_2 C_2 C_6(31)$ | $\tau C C_2 C_2 C_2(16)+\tau C C_2 C_2 C_2(34)+\tau C C_2 C_2 C_2(10)$ | $\nu C C_2(17)+\beta N C_2 C_2 C_2(22)+\beta C C_2 C_2(20)$ | $\nu C C_2 C_2 C_2(18)+\nu S C C_2 C_2(34)$ | $\beta C C_2 C_2 C_2(36)$ | $\nu C C_2 C_2 C_2(11)+\nu C C_2 N_2 N_2(20)+\nu C C_2 N_2 N_2(16)$ | $\beta C C_2 C_2 C_2(30)+\nu C C_2 N_2(22)$ | $\nu C C_2 C_2 C_2(14)+\nu C C_2 C_2 C_2(14)+\nu C C_2 C_2 C_2(14)$ | $\nu C C_2 N_2 C_2(20)+\nu C C_2 C_2 C_2(20)+\nu C C_2 C_2 C_2(20)$ | $\nu C C_2 C_2 C_2(18)+\nu C C_2 N_2 N_2(20)+\nu C C_2 N_2 N_2(20)$ | $\nu C C_2 C_2 N_2(18)+\nu C C_2 C_2 N_2(15)+\nu C C_2 C_2 N_2(15)$ | $\nu C C_2 C_2 N_2(18)+\nu C C_2 C_2 N_2(18)+\nu C C_2 C_2 N_2(18)$ | $\beta C C_2 N_2 C_2 C_2(18)+\nu C C_2 N_2 N_2(25)+\nu C C_2 N_2 N_2(25)$ | $\nu C C_2 C_2 C_2(18)$ | $\nu C C_2 C_2 C_2(18)$ | $\nu C C_2 C_2 C_2(18)$ |

$v$: Stretching, $\beta$: in-plane-bending, $\Gamma$: out-of-plane bending, $\tau$: Torsion, $w v$: very weak, $w$: week, $m$: medium, $s$: strong, $v s$: very strong.

Scaling factor: 0.9608.

Relative IR absorption intensities normalized with highest peak absorption equal to 100.

Relative Raman intensities calculated by Equation (1) and normalized to 100.

Total energy distribution calculated at B3LYP/6-311++G(d,p) level.
made in the present study. These vibrational assignments are further supported by literature [28] and TED output.

**C=C, C-C vibrations**

In the pyridine ring, the ν(C-C) stretching vibrations are usually occur in the ranges of 1590-1640, 1560-1580 and 1470-1510 cm⁻¹ [33]. The computed wavenumber for ν(C-C) modes are lies at 1563, 1542, 1240 and 1173 cm⁻¹ (mode nos: 12, 13, 22 and 25) with TED values. In the present study it has been established well and the FTIR band at 1549 cm⁻¹ and FT-Raman bands at 1241, 1195 cm⁻¹ are designated as νC-C vibrations. These assignments are find support from the literature [34] and also from TED values. The bands arising from βCCC and ΓCCC of pyridine moiety are ascribed to bands observed at 1031, 607 and 503 cm⁻¹ respectively in FTIR spectrum. These vibrational assignments find support from harmonic bands: 1017, 999, 608 and 507, 381, 163 cm⁻¹ (mode nos: 31, 33, 49 and 52, 57, 63) in addition to literature values [35].

The νCH modes are expected to appear in the range of 3100-3000 cm⁻¹ with multiple weak bands and the bands are not affected appreciably by the nature of the substituent’s [31,32]. The νC-H vibration of the thiophen ring is observed at 3171 cm⁻¹ in FT-IR and 3079 cm⁻¹ in FT-Raman spectra in accordance with the literature [20-22]. The harmonic values corresponding to νC-H are calculated in the range 3120-3078 cm⁻¹ (mode nos: 2-4) with TED values >96%. This indicates that these are highly pure stretching modes. The βC-H vibrations appear by sharp but weak to medium bands in the range 1100-1500 cm⁻¹ and the bands are not sensitive to the nature of substitutents. The ΓC-H deformation modes are expected to appear in the range 800-1000 cm⁻¹ [32]. The IR active βC-H/ΓC-H vibrations of T2CNH molecule are observed at 1218/897 cm⁻¹, respectively. The harmonic wavenumbers of these bands are 1219, 1059, 1015 and 891, 817 cm⁻¹ in good agreement with literature values [20-22].

The harmonic frequencies for νC-H, βC-H and ΓC-H modes in hydrozone linkage were assigned at 2919, 1315 and 910 cm⁻¹, respectively and these assignments are in line with assignments νC-H: 2901, βC-H: 1335, ΓC-H: 908 cm⁻¹ (mode nos: 9, 19, 37) are:

![Figure 2](image1.png)  
**Figure 2** The Theoretical and Experimental FT-IR spectra of T2CNH.

![Figure 3](image2.png)  
**Figure 3** The Theoretical and Experimental FT-Raman spectra of T2CNH.
The ring carbon-carbon stretching vibrations in thiophene ring are reported in the ranges of 1329-1431, 1420-1501 and 1419-1519 cm\(^{-1}\), respectively [20-22]. For the same mode the computed wavenumbers are: 1508 (C=C), 1490 (C=C) and 1402 cm\(^{-1}\) (C=C). These assignments are having considerable TED values ≥ 15% and its corresponding mode no: 14 is further supported by observed Raman band 1519 cm\(^{-1}\). The ßCCC mode of thiophene moiety is ascribed to mode no: 44 (718 cm\(^{-1}\)) and its TED value supports from TED values (30%, 43%). The ßCSC and ΓCSC vibrations are ascribed to wavenumbers: 586 cm\(^{-1}\) (mode nos: 63, 59) are assigned to τC\(_{9}\)-N\(_{11}\)-C\(_{14}\) modes. Similarly the τC\(_{9}\)-N\(_{11}\)-C\(_{14}\), τC\(_{9}\)-C\(_{9}\)-C\(_{13}\), τC\(_{9}\)-C\(_{9}\)-N\(_{11}\), τC\(_{9}\)-C\(_{9}\)-N\(_{11}\) modes are assigned to wavenumbers: 690, 381, 217, 217 cm\(^{-1}\) (mode nos: 47, 57, 61, 61).

### N-N vibrations

The νN-N stretching was observed at 1145 cm\(^{-1}\) in FTIR is undoubtedly assigned to c\(_{11}\)-N\(_{12}\)-N\(_{12}\) vibration and the value of this band is calculated at 1148 cm\(^{-1}\) (mode no: 26) with a TED of (60%) [28]. This assignment is well correlated with observed FT-Raman band 1149 cm\(^{-1}\). The in-plane bending vibrations of C\(_{2}\)-C\(_{9}\)-N\(_{11}\), C\(_{2}\)-N\(_{11}\)-N\(_{12}\), & C\(_{2}\)-N\(_{12}\)-N\(_{11}\) are assigned to wavenumbers: 791, 45 & 885, having considerable TED values (≥ 20%). The wavenumbers 163, 326 cm\(^{-1}\) (mode nos: 63, 59) are assigned to τC\(_{9}\)-N\(_{11}\)-N\(_{12}\)-C\(_{14}\), τC\(_{9}\)-C\(_{9}\)-N\(_{11}\) modes.

### C-S vibrations

In T2CNH the scaled wavenumbers 791 and 718 cm\(^{-1}\) (mode nos: 43 and 44) are assigned to vC\(_{9}\)-S\(_{1}\) and vC\(_{14}\)-S\(_{1}\) modes and are in agreement with literature [28].

### C=O vibrations

The C=O is formed by σπ-σπ bonding between carbon and oxygen atoms. Carbonyl (C=O) group stretching vibration is expected to appear in the region of 1680-1715 cm\(^{-1}\) [38]. In this study, the carbonyl group stretching vibration appear at 1670 cm\(^{-1}\) as strong band in FT-IR and at 1673 cm\(^{-1}\) as weak band in FT-Raman spectra. The values of νC=O band is calculated at 1688 cm\(^{-1}\) (mode no: 10) with a TED of 85%. The ßC=O and ΓC=O vibrations are assigned respectively to mode nos: 39 and 45, in which the predicted wavenumber related to ΓC=O mode is found to be in moderate agreement with the observed FTIR band at 700 cm\(^{-1}\).

### NLO Property

Analysis of organic compounds having conjugated n-electron systems and large hyperpolarizability using IR and Raman spectroscopy has evolved as a subject of scientific research. The application of the title molecule in the field of non-linear optics demands the investigation of its structural and bonding features.

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contribution to the hyperpolarizability enhancement by analyzing the vibrational modes using IR and Raman spectroscopy. The DFT/B3LYP/6-311++G(d,p) basis set has been used for the prediction of first hyperpolarizability.

The calculated first hyperpolarizability and the total molecular dipole moment of T2CNH is $1.5861 \times 10^{-30}$ Debye, respectively obtained by B3LYP/6-311++G(d,p) level of theory. The total dipole moment of the title molecule is moderately equal and $\beta_0$ value of T2CNH is 4 times greater than that of urea, hence the molecule T2CNH has considerable non-linear optical (NLO) activity and the hyperpolarizabilities of T2CNH are given in Table 3.

### NBO Analysis

This method gives information about the intra- and inter-molecular interactions among bonds. Furthermore, it provides a convenient basis for investigating the interactions in both filled and virtual orbital spaces along with charge transfer and conjugative interactions in molecular system [39]. The natural bonding orbital (NBO) analysis was performed for T2CNH using B3LYP/6-311++G(d,p) basis set in order to elucidate the intra-molecular, hybridization and delocalization of ED within T2CNH. The strong intramolecular hyperconjugative interaction of the $\sigma$ and $\pi$ electrons of C−C to the anti C−C bond of the pyridine ring leads to stabilization of some part of the pyridine ring. The NBO analysis has been carried out by B3LYP/6-311++G(d,p) basis set and the E(2) values and types of the transition are shown in Table 4.

![Figure 4](http://www.imedpub.com/archives-in-chemical-research/) The HOMO is located over the thiophene and hydrazone moieties. The LUMO is located over pyridine ring. The LUMO transition implies that an ED transfer to pyridine ring via hydrazone linkage. The LUMO transition energy was calculated by B3LYP/6-311++G(d,p) level of theory. The frontier molecular orbitals (FMOs) of T2CNH are listed in Table 5. The atomic compositions of FMOs are shown in Figure 4. The HOMO and LUMO energy gap is 4.025 eV, which reflects the chemical activity of the molecule. The HOMO and LUMO energy was calculated by B3LYP/6-311++G(d,p) level of theory. The frontier molecular orbitals (FMOs) of T2CNH are listed in Table 5. The atomic compositions of FMOs are shown in Figure 4. The HOMO and LUMO energy gap is 4.025 eV, which reflects the chemical activity of the molecule. The HOMO and LUMO energy gaps are predicted as -6.248 eV and -2.223 eV, respectively. The calculated HOMO-LUMO energy gap is 4.025 eV, which explains the eventual charge transfer taking place within the present molecule. The physico-chemical properties are also listed in Table 6.

### UV-Vis Spectral Analysis

The UV-Visible absorption spectrum of T2CNH was recorded in the range of 250-350 nm is shown in Figure 5. All the structures allow strong $\pi-\pi^*$ (or) $\sigma-\sigma^*$ transition in the UV-Vis region with high extinction coefficients. On the basis of fully optimized ground state structure at TD-DFT/B3LYP/6-311++G(d,p) calculation has been used to determine the low-lying excited states of T2CNH. The calculated results involving the vertical excitation energies, oscillator strength (f) and wavelength are carried out and compared with measured experimental wavelength. Typically, according to Franck-Condon principle, the maximum absorption peaks ($\lambda_{max}$) in a UV-Vis spectrum corresponds to vertical excitation. It is evident from the Table 7 that the calculated absorption maxima values have been found to be 332, 301 and

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### Table 3 The NLO measurements of T2CNH.

| Parameters          | B3LYP/6-311++G(d,p) | Debye  |
|---------------------|---------------------|--------|
| Dipole moment ( $\mu$ ) |                     |        |
| $\mu_x$             | 0.3145              |        |
| $\mu_y$             | -0.7701             |        |
| $\mu_z$             | 0.5380              |        |
| $\mu$               | 0.9906Debye         |        |
| Polarizability ( $\alpha_{ij}$ ) | $\times 10^{-30}$esu |        |
| $\alpha_{xx}$        | 330.88              |        |
| $\alpha_{yy}$        | -3.11               |        |
| $\alpha_{zz}$        | 168.52              |        |
| $\alpha_{xy}$        | -4.63               |        |
| $\alpha_{xz}$        | -0.11               |        |
| $\alpha_{yz}$        | 97.39               |        |
| $\alpha_{zz}$        | 0.5318x10^{-30}esu  |        |
| Hyperpolarizability ( $\beta_{ij}$ ) | $\times 10^{-30}$esu |        |
| $\beta_{xxx}$        | -1853.85            |        |
| $\beta_{xyy}$        | 229.60              |        |
| $\beta_{yyz}$        | -33.45              |        |
| $\beta_{yyy}$        | -129.96             |        |
| $\beta_{xxz}$        | 40.31               |        |
| $\beta_{xyz}$        | 21.11               |        |
| $\beta_{yzz}$        | 2.92                |        |
| $\beta_{zxx}$        | 54.46               |        |
| $\beta_{zyy}$        | -29.90              |        |
| $\beta_{zzx}$        | -38.55              |        |
| $\beta_{zzz}$        | 1.5861x10^{-30}esu  |        |

Standard value for urea ($\mu=1.3732$ Debye, $\beta_p=0.3728 \times 10^{-30}$ esu): esu-electrostatic unit

The larger E(2) value shows the intensive interaction between electron donors and electron acceptors. The strong intramolecular hyperconjugative interactions of the $\sigma$ and $\pi$ electrons of the C=C, C=N to the anti C=C, C=N bond of the ring as well as C=O group leads to stabilization of some part of the ring system in T2CNH. In the present study, the $\pi$-character of the bond plays an important role on comparing with $\sigma$ bond character. The hyper conjugative interactions $\pi(C_1-C_2)\rightarrow\pi^*(C_1-C_2)$, $\pi(C_1-C_2)\rightarrow\pi^*(C_1-C_2)$, $\pi(C_1-C_2)\rightarrow\pi^*(C_1-C_2)$, $\pi(C_1-C_2)\rightarrow\pi^*(C_1-C_2)$ and $\pi(C_1-C_2)\rightarrow\pi^*(C_1-C_2)$ transfer stabilization energy: 76.65, 66.02, 89.54, 122.13, 112.97 and 15.10 KJ/mol to the molecular system. The lone pair of sulphar, nitrogen and oxygen atoms play great role in T2CNH molecule. The $S_{12}$, $N_{14}$ & $O_{15}$ atoms transfer maximum energy 91.55, 190.41 and 118.20 KJ/mol to (C_4-C_5), (C_14-O_15) & (N_12-C_14) bonds, respectively. The maximum hyper conjugative E(2) energy of heteroatoms during the inter-molecular interaction leads the molecule towards medicinal and biological applications [28]. The bond $\sigma(C_6-H_6)$ transfer more energy (23.39 KJ/mol) to $\sigma^*(S_{1-C_2})$ bond on comparing with energy transfer (18.95 KJ/mol) from $\sigma(C_6-H_6)$ to $\sigma^*(S_{1-C_2})$. Hence the $v(S_{1-C_2})$ mode observe at higher frequency 791 cm$^{-1}$ (mode no: 43) than the $v(S_{1-C_2})$ mode (718 cm$^{-1}$/mode no: 44).
Type | Donor NBO (i) | ED/e | Acceptor NBO (j) | ED/e | $E^{\text{ii}}$ kJ/mol | $E(j)-E(i)$ a.u. | $F(i,j)$ a.u. 
--- | --- | --- | --- | --- | --- | --- | --- 
$\pi - \pi^*$ | BD (2) C2 - C3 | 1.795 | BD*(2) C4 - C5 | 0.309 | 69.58 | 0.28 | 0.06 
$\sigma - \sigma^*$ | BD (1) C3 - H8 | 1.972 | BD*(1) S1 - C2 | 0.028 | 23.39 | 0.73 | 0.06 
$\pi - \pi^*$ | BD (2) C4 - C5 | 1.846 | BD*(2) C2 - C3 | 0.351 | 66.02 | 0.30 | 0.06 
$\sigma - \sigma^*$ | BD (1) C4 - H7 | 1.976 | BD*(1) S1 - C5 | 0.017 | 18.95 | 0.75 | 0.05 

Table 4 The second order perturbation theory analysis of Fock Matrix in NBO basis for T2CNH.

| Occupancy | Orbital energies (a.u) | Orbital energies (eV) | Kinetic energies (a.u) 
--- | --- | --- | --- 
O$_{56}$ | -0.292 | -7.947 | 1.641 
O$_{57}$ | -0.284 | -7.740 | 1.641 
O$_{58}$ | -0.271 | -7.390 | 1.582 
O$_{59}$ | -0.269 | -7.342 | 2.186 
O$_{60}$ | -0.229 | -6.248 | 1.567 
V$_{61}$ | -0.081 | -2.223 | 1.590 
V$_{62}$ | -0.055 | -1.503 | 1.586 
V$_{63}$ | -0.055 | -1.503 | 1.424 
V$_{64}$ | -0.019 | -0.519 | 0.488 
V$_{65}$ | -0.009 | -0.255 | 0.535 

Table 5 The frontier molecular orbital of T$_2$CNH.

286 nm which correlates well with the experimental values 340 and 290 nm. The more intense band at 340 nm has maximum oscillator strength ($f$=0.6909), corresponds to HOMO-LUMO transition and is mostly characterized as n-π* type. This type of transition is attributed to the presence of large no of free lone pairs of electrons available on sulphar (S$_1$), Nitrogen (N$_{11}$, N$_{12}$) and oxygen (O$_{15}$) atoms. The experimental and theoretical UV-Vis absorption spectrum is shown in Figure 5. The density of states spectrum of T2CNH is shown in Figure 6. It was used to calculate group contributions to the molecular orbitals (HOMO and LUMO). DOS plot shows population analysis per orbital and demonstrates a simple view of the character of the molecular orbitals (MOs) in a certain energy range.

| Parameters | Values 
--- | --- 
HOMO | -6.248 eV 
LUMO | -2.223 eV 
Energy gap | 4.025 eV 
Ionization potential (IP) | 6.248 eV 
Electron affinity (EA) | 2.223 eV 
Electrophilicity Index (ω) | 2.562 
Chemical Potential (μ) | 7.359 
Electro negativity (χ) | -7.359 
Hardness (η) | -4.025 

Table 6 The Physico-Chemical properties of T$_2$CNH.
MEP Analysis

The molecular electrostatic potential (MEP) is widely used as a reactivity map displaying most probable regions for the electrophilic attack of charged part on organic molecule. MEP plot provides a simple way in predicting the interaction of different geometries. In order to predict the reactive sites for electrophilic and nucleophilic attacks of the T$_2$CNH, MEP was calculated with DFT/B3LYP/6-311++G(d,p) level of theory. The negative (red color) and positive (blue color) regions of MEP are related to electrophilic and nucleophilic reactivity respectively is shown in Figure 7. The negative region is located over the carbonyl group and the positive region is located over Hydrogen atom in the hydrazone linkage.

Mulliken Charges Analysis

The Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system, because the atomic charges should affect dipole moment, polarizability, electronic structure and more a lot of properties of molecular systems. The total atomic charges of T$_2$CNH are calculated by Mulliken population analysis with B3LYP/6-311++G(d,p) basis set and its values are listed in Table 8. The Mulliken atomic charge plot for T$_2$CNH is shown in Figure 8.

Table 7 The electronic transition of T$_2$CNH.

| Calculated at | Oscillator strength | Calculated Band gap (eV/nm) | Experimental Band gap (nm) | Type |
|---------------|---------------------|-----------------------------|---------------------------|------|
| B3LYP/6-311++G(d,p) |                     |                             |                           |      |
| Excited State 1 | Singlet-A (f=0.6909) | 3.7311 eV/332.30 nm | 340 | π-π* |
| 60 -> 61 | 0.6388 | -4.0254 |
| 60 -> 62 | 0.1325 | -4.7451 |
| Excited State 2 | Singlet-A (f=0.0043) | 4.1118 eV/301.54 nm | 59 | π-π* |
| 59 -> 61 | 0.6467 | -5.1187 |
| 59 -> 62 | 0.1819 | -5.8384 |
| Excited State 3 | Singlet-A (f=0.0126) | 4.3234 eV/286.77 nm | 290 | π-π* |
| 60 -> 62 | 0.4175 | -4.7451 |
| 60 -> 63 | 0.5580 | -4.8692 |

Figure 5 The Theoretical and Experimental UV-Visible spectra of T$_2$CNH.

Figure 6 The DOS spectrum of T$_2$CNH.

Figure 7 Molecular electrostatic potential map of T$_2$CNH.
atoms have the highest negative/positive charges, respectively among the other atoms in T2CNH due to the resonance.

**Thermodynamical Properties**

Several thermodynamic parameters have been calculated using DFT/B3LYP/6-311++G(d,p) basis set listed in Table 9. The thermodynamic parameters viz, entropy ($S^\circ_m$), enthalpy ($\Delta H^\circ_m$) and heat capacity at constant pressure ($C^{0}_{p,m}$) were calculated from the theoretical harmonic wavenumbers obtained from B3LYP/6-311++G(d,p) basis set in the range 100-1000 K and listed in Table 10. It is evident from the Table 10 that the thermodynamic parameters increase with rise of temperature due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between these thermodynamic parameters and temperature were fitted by parabolic formula and the regression coefficient is also given in the parabolic equation. The correlation relation between the thermodynamic parameters and temperature are as follows:

$$C^{0}_{p,m} = 4.44266 + 0.01876T + 1.6571 \times 10^{-5} T^2 \quad (R^2=0.99929)$$

$$S^\circ_m = 1.35549 + 0.00572T + 5.0560 \times 10^{-5} T^2 \quad (R^2=0.99997)$$

$$\Delta H^\circ_m = 3.15466 + 0.01332T + 1.1767 \times 10^{-5} T^2 \quad (R^2=0.99944)$$

The correlation graphs between various thermodynamic functions and temperature are graphically presented in Figure 9.

**Conclusion**

The complete vibrational analysis has been performed to using quantum chemical calculation at DFT method for the first time to the title molecule T$_2$CNH. The calculated bond parameters are good agreement with the related single crystal X-ray diffraction (XRD) data. In T$_2$CNH, the thiophene and hydrazone moieties are co-planar, which shows a good conjunction between p-orbitals of all atoms of thiophene and hydrazone moieties. The vibrational atoms have the highest negative/positive charges, respectively among the other atoms in T2CNH due to the resonance.

**Table 8 The Mulliken atomic charges of T$_2$CNH.**

| Atoms | Charges |
|-------|---------|
| S1    | -0.6516 |
| C2    | 0.2759  |
| C3    | 1.9917  |
| C4    | -1.2036 |
| C5    | 0.4451  |
| C6    | 0.2687  |
| C7    | 0.1582  |
| C8    | 0.2452  |
| C9    | -1.7721 |
| H10   | 0.1263  |
| N11   | 0.1794  |
| N12   | -0.0550 |
| N13   | -0.0964 |
| N14   | -0.2925 |
| N15   | 0.9920  |
| N16   | 0.1758  |
| N17   | 0.1784  |
| N18   | 0.1592  |
| N19   | -0.0124 |
| H20   | 0.1582  |
| H21   | 0.14465 |
| H22   | 0.2477  |
| H23   | 0.2280  |
| H24   | 0.1897  |
| H25   | 0.1903  |
| C21   | -0.0124 |
| C22   | -0.0964 |
| C23   | -0.0550 |
| C24   | 0.9920  |
| C25   | 0.1758  |
| C26   | 0.1784  |
| C27   | 0.1592  |
| C28   | 0.14465 |
| C29   | 0.0967  |

**Table 9 The calculated total energy (a.u), zero point vibrational energies (kcal/mol), rotational constants (GHz) and entropy (cal/mol K$^{-1}$) for T$_2$CNH.**

| Parameters                  | B3LYP/6-311++G(d,p) |
|-----------------------------|--------------------|
| Total Energies              | -1062.41677        |
| Zero-point Energy           | 114.99338 (Kcal/Mol)|
| Rotational constants (GHz)  | 1.78813            |
| Entropy                     | 0.15572            |
| Entropy                     | 0.14465            |
| Total Translational         | 122.336            |
| Total Rotational            | 42.214             |
| Total Vibrational           | 33.345             |
| Vibrational                 | 46.777             |

**Table 10 Thermodynamic properties of T2CNH at different temperatures.**

| T (K) | S (Jmol$^{-1}$K$^{-1}$) | Cp (Jmol$^{-1}$K$^{-1}$) | ddH (kJmol$^{-1}$) |
|-------|------------------------|--------------------------|-------------------|
| 100   | 349.07                 | 100                      | 6.95              |
| 200   | 436.15                 | 159.71                   | 19.86             |
| 298.15| 511.96                 | 224.53                   | 38.7              |
| 300   | 513.36                 | 225.74                   | 39.12             |
| 400   | 586.95                 | 287.34                   | 64.85             |
| 500   | 656.77                 | 338.54                   | 96.24             |
| 600   | 722.24                 | 379.34                   | 132.21            |
| 700   | 783.25                 | 411.8                    | 171.83            |
| 800   | 840.01                 | 438.01                   | 214.36            |
| 900   | 892.88                 | 459.52                   | 259.27            |
| 1000  | 942.25                 | 477.43                   | 306.15            |

**Figure 8** The Mulliken atomic charges of T$_2$CNH.

**Figure 9** The thermodynamic properties of T2CNH at different temperatures.
data of T2CNH are well supported by the harmonic and related literature values. The β0 value of T2CNH molecule is found to be $1.5861 \times 10^{-30}$ esu, which is four time greater than that of urea. The NBO result reflects the charge transfer with in the molecule and the maximum energy takes place during π-π* transition. The Homo-Lumo band gap was calculated about 4.025 eV, which leads the T, CNH molecule to become less stable and more reactive. The recorded UV-Vis spectral values are agree well with calculated values. MEP surface predict the reactive sites for electrophilic and nucleophilic attack. In addition, Mulliken atomic charges, zero point energy and thermodynamic properties are also calculated.
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