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

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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 thermodymanic properties were also calculated.

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

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Introduction

Generally, Pyridine ring is a heterocyclic organic compound with the chemical formula C_5H_5N. 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 tripelennamine 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 >C=N-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-l) methylene)benzene-1,2-diamine. The observed FT-IR and FT-Raman spectral values were compared with the calculated wave numbers. 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, Homo-Lumo energy gap was calculated and furthermore, the MEP and thermodynamic properties were also calculated.

Computational Details

The entire theoretical calculations were performed DFT method at B3LYP/6-311++G(d,p) basis set to using Gaussian 03W [15] program package, invoking gradient geometry optimization [15,16]. The geometrical parameters were used in the vibrational frequency calculations at the same level to characterize all the stationary points as minima. The vibrationally averaged nuclear positions of T2CNH were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The vibrational modes were assigned on the basis of TED analysis using VEDA4 program package [17]. The Raman activity was calculated by using Gaussian 03W package and the activity was transformed into Raman intensity using Raint program [18] by the expression:

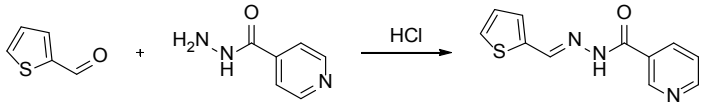
$$I_i = 10^{-12} \times (v_o - v_i)^4 \times \frac{1}{v_i} \times RA_i \quad (1)$$

Where Ii is the Raman intensity, RAi is the Raman scattering activities, vi is the wavenumber of the normal modes and v_0 denotes the wavenumber of the excitation laser [19].

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.



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 C_2-S_1 is expected to be shorter than the C_5-S_1 bond length, since the hydrozone moiety is attached with C_2 atom and their corresponding bond distances are 1.750 and 1.728Å. The bond lengths of C_2=C_3, C_3-C_4, C_4=C_5 are 1.377, 1.418, 1.369Å and the bond angles of C2-C3-C4, C3-C4-C5 are 113.02°, 113.03°. The bond angles S_1-C_2-C_3 and S_1-C_5-C_4 are differ by ~1° which is due to the shortening of bond distance between S_1 and C_2 atoms. These values are particularly in good agreement with the values of anti thiophen-2-aldehyde [20] and thiophen-2-carbohydrazide [21]. Furthermore, these values are also find support from literature [22]. The dihedral angles of S_1-C_2-C_9-N_{11}/ S_1-C_2-C_9-$H_1$0 and C_3-C_2-C_9-N_{11}/C_3-C_2-C_9-H_{10} are -179.96°/-0.07° and 0.03°/+179.93°, respectively, which shows that the thiophen and hydrozone moieties of T2CNH are co-planar. Since there is a good conjugation between p-orbitals of all atoms of thiophen and hydrazone 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 hydrozone 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 C_1 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

Table 1 The optimized bond parameters of T_2CNH.

Bond Parametres Bond Lengths (Å)	B3LYP/6-311++G(d,p)	XRD [a,b,c]
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[b]
C9-H10	1.097	0.930[c]
C9-N11	1.282	1.266[c]
N11-N12	1.357	1.375[c]
N12-H13	1.016	0.860[c]
N12-C14	1.385	1.354[c]
C14-O15	1.213	1.224[c]
C16-C17	1.399	1.384[c]
C16-C18	1.397	1.371[c]
C17-N19	1.335	1.334[c]
C17-H20	1.087	0.930[c]
C18-C21	1.387	1.368[c]
C18-H22	1.083	0.930[c]
N19-C23	1.335	1.337[c]
C21-C23	1.395	1.368[c]
C23-H25	1.086	0.930[c]
Bond Angles (°)		
C2-S1-C5	91.57	92.00[a], 91.81[b]
S1-C2-C3	110.68	111.80[a]
C2-C3-C4	113.02	112.20[a], 114.72[b]
C2-C3-H8	122.16	129.20[a]
C3-C4-C5	113.03	112.05[b]
S1-C5-C4	111.68	112.13[b]
N12-C14-C16	114.21	114.95[c]
O15-C14-C16	122.13	121.48[c]
C16-C17-N19	123.88	122.05[c]
C16-C17-H20	120.91	120.03[c]
N19-C17-H20	115.16	118.20[c]
C16-C18-C21	118.94	118.91[c]
C16-C18-H22	119.08	120.50[c]
C21-C18-H22	121.96	120.30[c]
C17-N19-C23	117.47	117.44[c]
C18-C21-C23	118.58	118.58[c]
C18-C21-H24	121.13	120.71[c]
C23-C21-H24	120.27	120.70[c]
N19-C23-C21	123.40	123.64[c]
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	
H7-C4-C5-S1	179.99	
H7-C4-C5-H6	0.01	
C2-C9-N11-N12	179.45	
H10-C9-N11-N12	-0.43	
C9-N11-N12-H13	1.93	
C9-N11-N12-C14	175.56	
N11-N12-C14-O15	-2.82	
N11-N12-C14-C16	177.89	
H13-N12-C14-O15	170.80	
H13-N12-C14-C16	-8.47	
N12-C14-C16-C17	-28.41	
N12-C14-C16-C18	154.27	
O15-C14-C16-C17	152.29	
O15-C14-C16-C18	-25.01	
C14-C16-C17-N19	-178.88	
C14-C16-C17-H20	-0.97	
C18-C16-C17-N19	-1.57	

[a]Brathen O, Kveseth K, Nielsen 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 vN-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 vCH, 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.

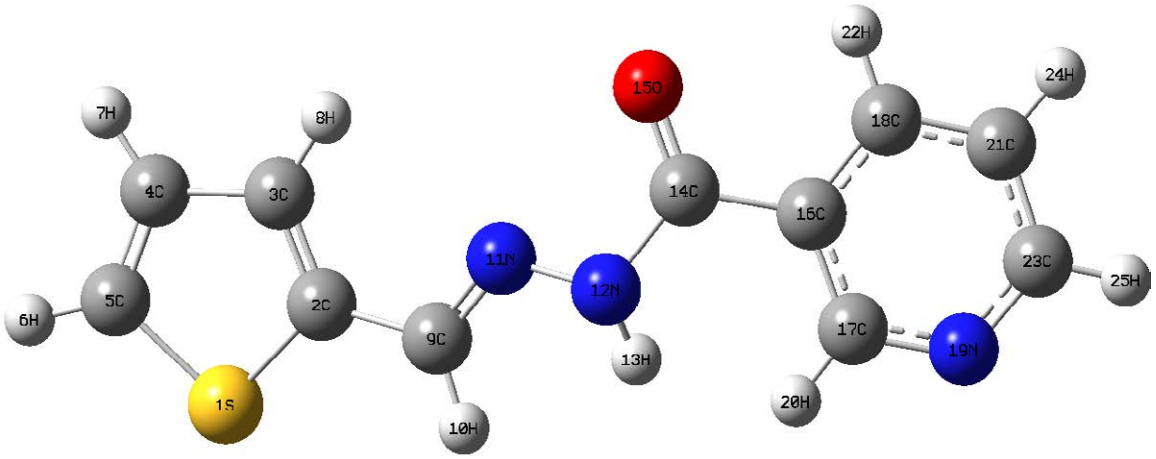


Figure 1 The Optimized structure of (E)-N′-(thiophen-2-ylmethylene) nicotinohydrazide (T2CNH).

Table 2 The experimental and calculated frequencies of T_2CNH using B3LYP/6-311++G(d,p) level of basis set [harmonic frequencies (cm^{-1}), IR, Raman intensities (Km/mol), reduced masses (amu) and force constants (mdynA°$^{-1}$)].

Mode No	Calculated Frequencies (cm^{-1})		Observed Frequencies cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Consts	Vibrational assignments≥10% (TED)[d]
	Un Scaled	Scaled[a]	FT-IR	FT-Raman	Abs.	Rel.[b]	Abs.	Rel.[c]			
1	3503	3365	3401 w		7.42	2.06	134.41	1.67	1.08	7.78	$vN_{12}H_{13}$(100)
2	3247	3120	3171 w		1.23	0.34	101.27	1.26	1.10	6.82	vC_5H_6(94)
3	3223	3096			0.57	0.16	34.50	0.43	1.10	6.70	vC_3H_8(97)
4	3204	3078		3079 w	6.29	1.75	62.54	0.78	1.09	6.59	vC_4H_7(96)
5	3202	3076			7.00	1.94	72.48	0.90	1.10	6.62	$vC_{18}H_{22}$(99)
6	3187	3062	3059 w		9.14	2.54	84.20	1.05	1.09	6.53	$vC_{21}H_{24}$(95)
7	3156	3032			10.92	3.03	72.05	0.89	1.09	6.39	$vC_{23}H_{25}$(92)
8	3139	3016			29.24	8.12	29.47	0.37	1.09	6.32	$vC_{17}H_{20}$(99)
9	3019	2901			42.64	11.84	29.11	0.36	1.09	5.83	vC_9H_{10}(100)
10	1757	1688	1673 s	1670 w	360.16	100.00	392.18	4.87	11.08	20.16	$vO_{15}C_{14}$(85)
11	1656	1591	1592 s	1589 s	15.73	4.37	8057.31	100.00	7.23	11.68	$vN_{11}C_9$(75)+$\beta H_{10}C_9N_{11}$(20)
12	1627	1563			32.79	9.10	1339.53	16.63	5.75	8.96	$vC_{18}C_{21}$(30)+$vN_{19}C_{23}$(30)+$\beta C_{21}C_{23}N_{19}$(25)
13	1605	1542	1549 w		6.21	1.73	25.40	0.32	5.21	7.91	$vC_{21}C_{23}$(31)+$vC_{16}C_{18}$(27)+$\beta C_{17}N_{19}C_{23}$(10)
14	1570	1508		1519 w	217.56	60.41	126.25	1.57	3.38	4.91	vC_2C_3(28)+$\beta H_{13}N_{12}N_{11}$(22)+vC_4C_5(13)+vC_2C_9(11)
15	1551	1490			202.85	56.32	2133.94	26.48	2.19	3.10	vC_2C_3(14)+$\beta H_{13}N_{12}N_{11}$(41)+vC_4C_5(12)
16	1506	1447	1425 m	1429 m	26.23	7.28	58.60	0.73	2.15	2.87	$\beta H_{24}C_{21}C_{23}$(27)+$\beta H_{20}C_{17}C_{16}$(25)
17	1459	1402			8.66	2.41	4817.87	59.80	4.83	6.07	vC_2C_3(13)+vC_4C_5(32)+$\beta H_7C_4C_5$(14)+vC_3C_4(15)
18	1448	1391			26.37	7.32	62.23	0.77	2.18	2.69	$\beta H_{25}C_{23}N_{19}$(43)+$\beta C_{16}C_{17}N_{19}$(23)
19	1390	1335			52.04	14.45	1478.54	18.35	1.75	1.99	vC_4C_5(13)+$\beta H_{10}C_9N_{11}$(38)+$\beta H_6C_5C_4$(13)
20	1387	1333			16.34	4.54	60.17	0.75	2.08	2.36	$\beta H_{10}C_9N_{11}$(25)+$\beta H_6C_5C_4$(15)+vC_3C_4(18)
21	1362	1308	1290 s	1300 m	0.98	0.27	2.27	0.03	1.31	1.43	$\beta H_{20}C_{17}C_{16}$(45)+$\beta H_{22}C_{18}C_{21}$(23)
22	1291	1240		1241 w	19.71	5.47	141.74	1.76	7.28	7.15	$vN_{19}C_{23}$(43)+$vC_{16}C_{18}$(27)
23	1268	1219	1218 m	1225 w	94.23	26.16	45.69	0.57	1.54	1.46	$\beta H_7C_4C_5$(23)+$\beta H_8C_3C_4$(29)+$\beta H_6C_5C_4$(13)
24	1265	1215			221.71	61.56	2432.18	30.19	2.39	2.25	$vC_{14}C_{16}$(22)
25	1221	1173		1195 w	39.47	10.96	610.76	7.58	1.60	1.40	$vC_{18}C_{21}$(11)+$\beta H_{24}C_{21}C_{23}$(17)+$\beta H_{25}C_{23}N_{19}$(30)
26	1195	1148	1145 m	1149 w	87.67	24.34	456.90	5.67	3.39	2.85	$vN_{11}N_{12}$(60)
27	1142	1097		1096 w	146.68	40.73	527.62	6.55	2.70	2.07	vC_2C_9(10)+$vN_{12}C_{14}$(40)
28	1134	1090			69.91	19.41	242.18	3.01	1.45	1.10	$\beta H_{24}C_{21}C_{23}$(20)+$\beta C_{16}C_{17}N_{19}$(12)+$\beta H_{22}C_{18}C_{21}$(36)
29	1102	1059			7.47	2.07	295.96	3.67	1.26	0.90	vC_4C_5(15)+$\beta H_7C_4C_5$(22)+$\beta H_6C_5C_4$(47)
30	1086	1044			5.12	1.42	134.46	1.67	3.17	2.21	$vN_{11}N_{12}$(24)+$vN_{12}C_{14}$(16)
31	1058	1017	1031 w	1030 w	1.76	0.49	393.20	4.88	3.19	2.11	$\beta C_{16}C_{18}C_{21}$(45)

32	1056	1015			7.59	2.11	414.19	5.14	1.76	1.15	$\beta H_7C_4C_5(14)+\beta H_8C_3C_4(27)+\nu C_3C_4(35)$
33	1039	999			11.95	3.32	318.45	3.95	4.30	2.73	$\beta C_{17}N_{19}C_{23}(32)+\beta C_{21}C_{23}N_{19}(15)+\beta C_{18}C_{21}C_{23}(25)$
34	1014	974			2.23	0.62	6.67	0.08	1.38	0.83	$\tau H_{22}C_{18}C_{21}H_{24}(75)+\Gamma C_{23}C_{21}N_{19}H_{25}(18)$
35	987	949	948 w	955 w	0.58	0.16	8.33	0.10	1.43	0.82	$\Gamma C_{23}C_{21}N_{19}H_{25}(50)+\Gamma C_{17}C_{16}N_{19}H_{20}(12)+\Gamma C_{18}C_{16}C_{21}H_{22}(30)$
36	947	910			1.90	0.53	6.99	0.09	1.39	0.73	$\Gamma C_{17}C_{16}N_{19}H_{20}(71)$
37	945	908		904 w	9.84	2.73	50.68	0.63	1.50	0.79	$\Gamma H_{10}C_9N_{11}H_{12}(80)$
38	928	891	897 w		0.39	0.11	6.15	0.08	1.38	0.70	$\tau H_6C_5C_4H_7(46)+\Gamma C_3C_2C_4H_8(32)$
39	921	885			38.10	10.58	86.38	1.07	7.12	3.56	$\beta N_{12}C_{14}O_{15}(20)+\beta C_{14}N_{12}N_{11}(25)$
40	861	827	846 w		31.22	8.67	114.39	1.42	4.31	1.88	$\beta C_4C_5S_1(80)$
41	851	817			8.44	2.34	1.04	0.01	1.29	0.55	$\tau H_6C_5C_4H_7(36)+\Gamma C_3C_2C_4H_8(55)$
42	841	808			13.98	3.88	48.48	0.60	1.97	0.82	$\tau H_{22}C_{18}C_{21}H_{24}(17)+\Gamma C_{23}C_{21}N_{19}H_{25}(12)+\Gamma C_{18}C_{16}C_{21}H_{22}(32)+\Gamma O_{15}C_{16}N_{12}C_{14}(12)$
43	823	791			25.89	7.19	107.27	1.33	4.43	1.77	$\nu C_2C_3(10)+\beta C_2C_9N_{11}(20)+\nu S_1C_2(17)$
44	747	718			3.22	0.89	221.87	2.75	7.15	2.35	$\beta C_2C_3C_4(57)+\nu S_1C_2(23)$
45	739	710	700 w		31.92	8.86	64.22	0.80	2.76	0.89	$\Gamma C_{18}C_{16}C_{21}H_{22}(25)+\Gamma O_{15}C_{16}N_{12}C_{14}(50)$
46	724	695			21.84	6.06	20.02	0.25	4.31	1.33	$\beta C_{21}C_{23}N_{19}(17)+\tau C_{16}C_{17}C_{23}N_{19}(16)+\tau C_{16}C_{18}C_{23}C_{21}(16)+\tau C_{18}C_{21}N_{19}C_{23}(10)$
47	718	690			16.37	4.54	7.30	0.09	3.96	1.20	$\tau C_{16}C_{17}C_{23}N_{19}(27)+\tau C_{16}C_{18}C_{23}C_{21}(22)+\tau C_{18}C_{21}N_{19}C_{23}(16)$
48	706	679		652 w	75.61	20.99	10.36	0.13	1.17	0.34	$\tau H_6C_5C_4H_7(13)+\tau H_6C_5S_1C_2(81)$
49	633	608	607 s		4.00	1.11	49.48	0.61	7.72	1.82	$\beta C_{16}C_{17}N_{19}(15)+\beta C_{17}N_{19}C_{23}(15)+\beta C_{18}C_{21}C_{23}(41)$
50	610	586			2.58	0.72	360.42	4.47	9.05	1.98	$\beta C_2S_1C_5(63)$
51	586	563			1.22	0.34	16.70	0.21	3.25	0.66	$\tau C_3C_2C_4H_5(79)$
52	528	507	503 m		15.76	4.38	167.78	2.08	3.01	0.49	$\beta C_{16}C_{14}N_{12}(22)+\tau H_{13}N_{12}C_{14}C_{16}(22)+\Gamma C_{14}C_{16}C_{18}C_{17}(10)$
53	508	488			44.93	12.47	72.78	0.90	1.60	0.24	$\tau H_{13}N_{12}C_{14}C_{16}(61)$
54	492	472			0.31	0.09	8.91	0.11	4.01	0.57	$\tau C_2S_1C_4C_5(65)$
55	451	433			0.46	0.13	24.54	0.30	7.97	0.95	$\beta C_2C_9N_{11}(14)+\nu S_1C_2(12)+\beta C_{17}C_{16}C_{18}(10)+\beta C_9C_2S_1(12)+\beta C_{14}N_{12}N_{11}(11)$
56	419	402			7.99	2.22	9.91	0.12	4.68	0.48	$\tau C_{16}C_{17}C_{23}N_{19}(15)+\tau C_{16}C_{18}C_{23}C_{21}(31)$
57	396	381			4.89	1.36	11.97	0.15	3.36	0.31	$\tau C_{16}C_{18}C_{23}C_{21}(16)+\tau C_{18}C_{21}N_{19}C_{23}(34)+\Gamma C_{14}C_{16}C_{18}C_{17}(10)$
58	379	364			1.32	0.37	1.86	0.02	8.03	0.68	$\nu C_{14}C_{16}(17)+\beta N_{12}C_{14}O_{15}(22)+\beta C_{17}C_{16}C_{18}(20)$
59	340	326			1.88	0.52	29.62	0.37	5.99	0.41	$\tau C_2S_1C_4C_5(18)+\tau C_2C_9N_{11}N_{12}(34)$
60	264	253			13.84	3.84	34.50	0.43	4.73	0.19	$\beta C_{14}C_{16}C_{18}(36)$
61	226	217		224 w	11.59	3.22	71.81	0.89	3.69	0.11	$\tau C_5S_1C_2C_9(11)+\Gamma C_{16}C_{14}N_{12}N_{11}(20)+\tau C_3C_2C_9N_{11}(16)$
62	213	205		191 w	1.15	0.32	136.24	1.69	10.18	0.27	$\beta C_9C_2S_1(30)+\beta C_{14}N_{12}N_{11}(22)$
63	170	163			11.98	3.33	135.90	1.69	4.69	0.08	$\tau C_9N_{11}N_{12}C_{14}(20)+\Gamma C_{14}C_{16}C_{18}C_{17}(14)+\tau C_3C_2C_9N_{11}(13)$
64	130	125			1.52	0.42	83.59	1.04	5.74	0.06	$\tau C_9N_{11}N_{12}C_{14}(25)+\tau C_5S_1C_2C_9(37)+\Gamma C_{14}C_{16}C_{18}C_{17}(10)$
65	120	115			6.55	1.82	60.10	0.75	5.71	0.05	$\beta C_2C_9N_{11}(18)+\beta C_{16}C_{14}N_{12}(18)+\beta C_9C_2S_1(17)+\Gamma C_{14}C_{16}C_{18}C_{17}(14)$
66	64	61		80 m	5.89	1.63	381.03	4.73	5.90	0.01	$\tau C_5S_1C_2C_9(12)+\tau C_{18}C_{16}C_{14}N_{12}(45)+\tau C_3C_2C_9N_{11}(15)$
67	46	45			0.73	0.20	161.56	2.01	6.68	0.01	$\beta C_2C_9N_{11}(16)+\beta C_{16}C_{14}N_{12}(14)+\beta C_9N_{11}N_{12}(20)+\beta C_{14}N_{12}N_{11}(22)$
68	32	31			1.86	0.52	329.50	4.09	5.69	0.00	$\tau C_2C_9N_{11}N_{12}(18)+\tau C_{18}C_{16}C_{14}N_{12}(15)+\tau C_{16}C_{14}N_{12}N_{11}(49)$
69	27	26			0.47	0.13	967.33	12.01	5.46	0.00	$\tau C_9N_{11}N_{12}C_{14}(18)+\tau C_{18}C_{16}C_{14}N_{12}(25)+\tau C_3C_2C_9N_{11}(18)$

ν: Stretching, β: in-plane-bending, Γ: out-of-plane bending, τ- Torsion, vw: very week, w:week, m:medium, s:strong, vs: very strong.
[a]Scaling factor: 0.9608.
[b]Relative IR absorption intensities normalized with highest peak absorption equal to 100.
[c]Relative Raman intensities calculated by Equation (1) and normalized to 100.
[d]Total energy distribution calculated at B3LYP/6-311++G(d,p) level.

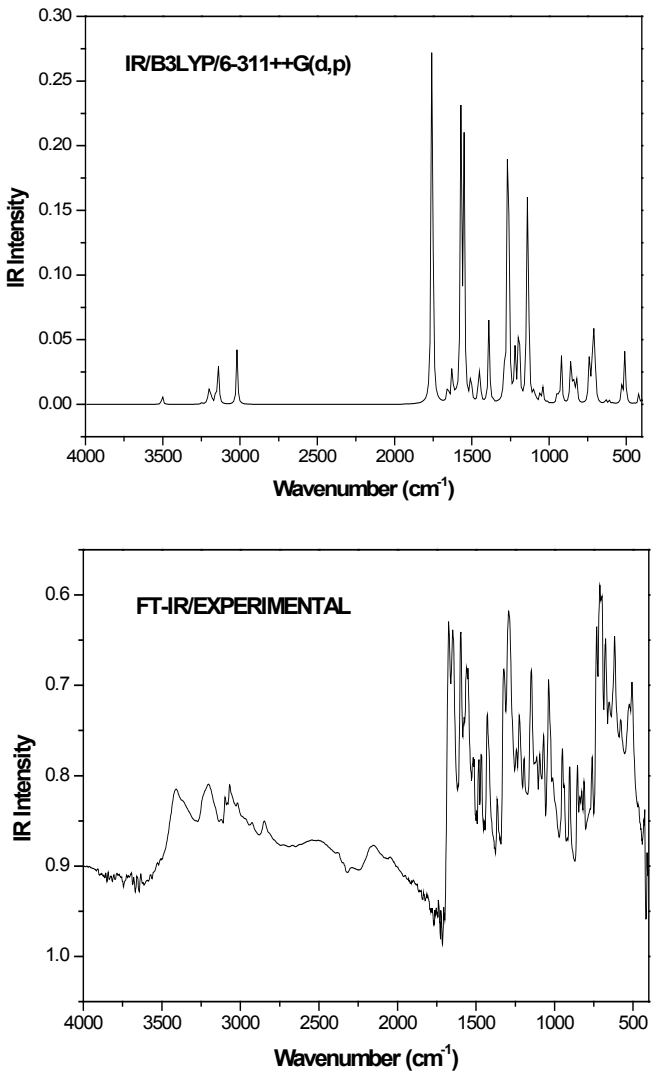


Figure 2 The Theoretical and Experimental FT-IR spectra of T_2CNH.

The vCH 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 vC-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 vC-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 vC-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 vC-H: 2901, βC-H: 1335, ΓC-H: 908 cm^{-1} (mode nos: 9, 19, 37) are 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].

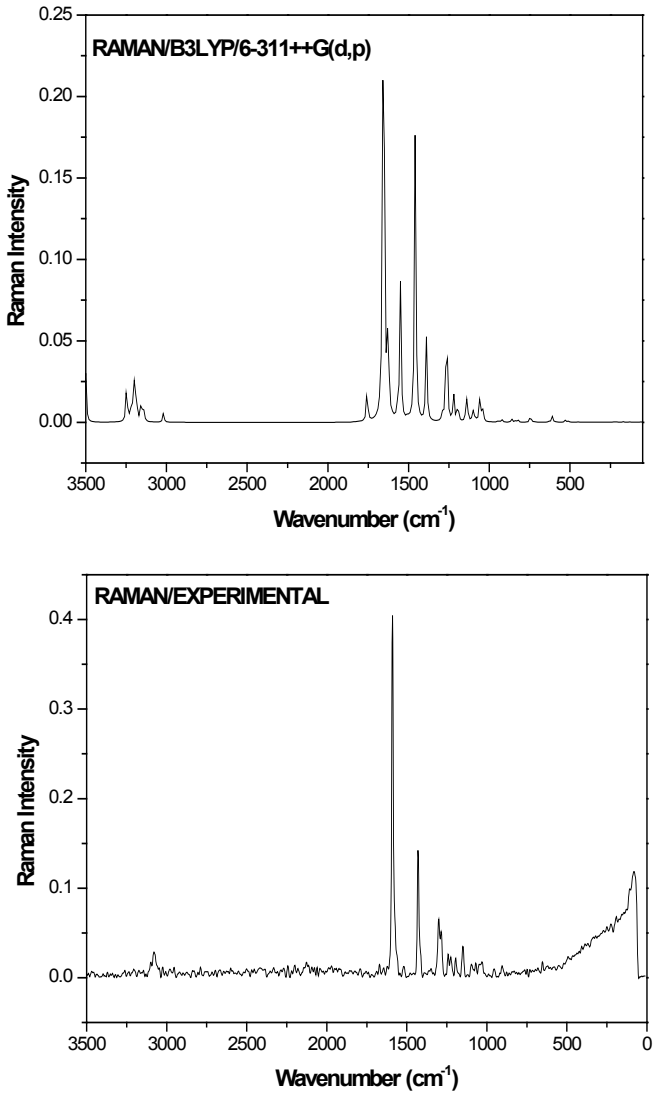


Figure 3 The Theoretical and Experimental FT-Raman spectra of T_2CNH.

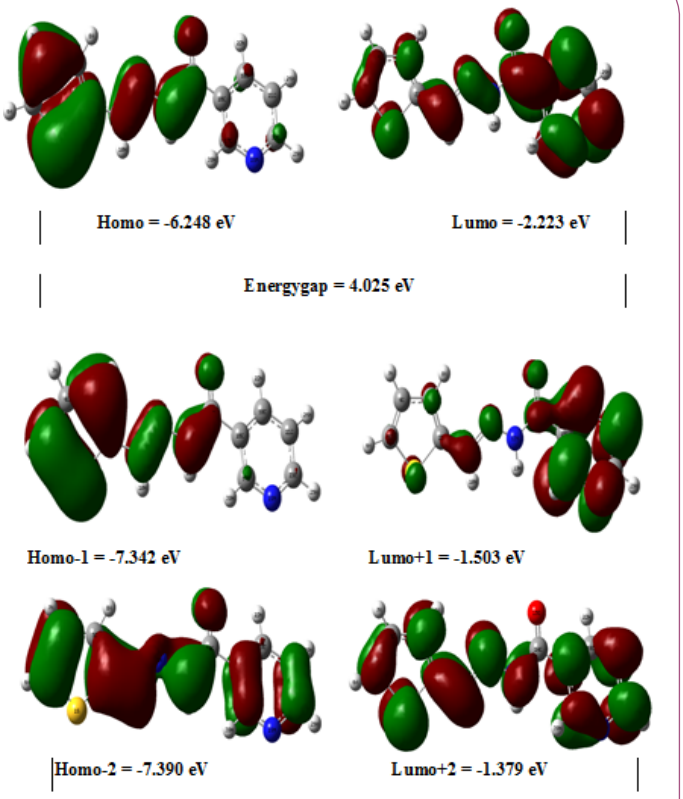


Figure 4 The frontier molecular orbitals for T_2CNH.

The ring carbon-carbon stretching vibrations in thiophen 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 βCCC mode of thiophene moiety is ascribed to mode no: 44 (718 cm^{-1}), this supported by TED value (57%) also. The mode nos: 27 and 24 are attributed to νC_2-C_9 and νC_{14}-C_{16} mode and are in agreement with literature [28].

C=N, C-N vibrations

The identifications of C=N and C-N vibrations is a difficult task, since the mixing of vibrations is possible in this region [36]. However, with the help of Gauss View (3.0) software and TED results, those vibrations are described and assigned in this study. The C=N and C-N stretching vibrations appear in the ranges of 1670-1600 cm^{-1} and 1382-1266 cm^{-1} respectively [36]. In hydrozone linkage, the νC9=N11 and νC14-N12 stretching vibrations are assigned respectively at 1592 cm^{-1} (FTIR) /1589 cm^{-1} (FT-Raman) and at 1096 cm^{-1} (FT-Raman). The TED results show that these vibrations are mixed with βHCN and νC-C modes and their corresponding harmonic frequencies are 1591 (mode no: 11) and 1097 cm^{-1} (mode no: 27) well correlated with experimental observations. These vibrational assignments are also supported by literature [28] in addition to TED output (75% and 40%).

In pyridine ring, the harmonic/observed bands at 1563 (mode no: 12), 1240 (mode no: 22)/1241 cm^{-1} in FT-Raman spectrum can be assigned to C-N stretching vibration and TED also predict that these vibrations are mixed with νC-C modes. These assignments are in good agreement with our earlier study [28] and also find support from TED values (30%, 43%). The βC_{21}-C_{23}-N_{19}, βC_{16}-C_{17}-N_{19}, βC_{17}-N_{19}-C_{23} and βC_2-C_9=N_{11}, βC_{16}-C_{14}-N_{12} deformations belong to pyridine and hydrozone moieties, respectively assigned to 1563, 1391, 999 and 791, 507 cm^{-1} (mode nos: 12, 18, 33 and 43, 52). Similarly the $\tau C_{16}C_{17}C_{23}N_{19}$, $\tau C_{18}C_{21}N_{19}C_{23}$, $\tau C_3C_2C_9N_{11}$, $\Gamma C_{16}C_{14}N_{12}N_{11}$ 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 νN_{11}-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_9=N_{11}-N_{12} & C_{14}-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_2-C_9=N_{11}-N_{12} modes.

C-S vibrations

In T2CNH the scaled wavenumbers 791 and 718 cm^{-1} (mode nos: 43 and 44) are assigned to νC-S modes of thiophen ring moiety. This assignment is in agreement with the assignments proposed by various authors [20,21]. This mode is well known to mix with neighboring modes (νCC, βCCN/mode no: 43 and βCCC/mode no: 44) as reported in the literature [37]. The harmonic frequencies of βCSC and ΓCSC vibrations are ascribed to wavenumbers: 586 cm^{-1} (mode no: 50) and 125 cm^{-1} (mode no: 64) with 62% and 37% of TED values, respectively. Further the wavenumbers 827 cm^{-1} (mode no: 40) and 205 cm^{-1} (mode no: 62) are assigned to $\beta C_4C_5S_1$ and $\beta C_9C_2S_1$ modes, respectively, which are in line with the observed bands (846 cm^{-1}: FTIR and 191 cm^{-1}: FT-Raman) in addition to support the TED values [80% and 30%].

C=O vibrations

The C=O is formed by Pπ-Pπ 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 βC=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 π-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

contributing 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 × 10^{-30} esu, 0.9906 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 β0 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 intra-molecular hyperconjugative interaction of the σ and π 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.**

Table 3 The NLO measurements of T_2CNH.

Parameters	B3LYP/6-311++G(d,p)
***Dipole* moment (μ)**	**Debye**
μ_x	0.3145
μ_y	-0.7701
μ_z	0.5380
μ	0.9906**Debye**
Polarizability (α_0)	**× 10^{-30}esu**
α_{xx}	330.88
α_{xy}	-3.11
α_{yy}	168.52
α_{xz}	-4.63
α_{yz}	-0.11
α_{zz}	97.39
α_0	0.5318x10^{-30}esu
***Hyperpolarizability* (β_0)**	**× 10^{-30}esu**
β_{xxx}	-1853.85
β_{xxy}	229.60
β_{xyy}	-33.45
β_{yyy}	-129.96
β_{xxz}	40.31
β_{xyz}	21.11
β_{yyz}	2.92
β_{xzz}	54.46
β_{yzz}	-29.90
β_{zzz}	-38.55
β_0	1.5861x10^{-30}esu

Standard value for urea (**μ**=1.3732 Debye, **β_0**=0.3728 × 10^{-30} esu): **esu**-electrostatic unit

The larger E(2) value shows the intensive interaction between electron donors and electron acceptors. The strong intra-molecular hyper conjugative interactions of the σ and π 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 T_2CNH. In the present study, the π-character of the bond plays an important role on comparing with σ bond character. The hyper conjugative interactions $\pi(C_2\text{-}C_3)\rightarrow\pi^*(C_9\text{-}N_{11})$, $\pi(C_4\text{-}C_5)\rightarrow\pi^*(C_2\text{-}C_3)$, $\pi(C_{16}\text{-}C_{17})\rightarrow\pi^*(C_{18}\text{-}C_{21})$, $\pi(C_{18}\text{-}C_{21})\rightarrow\pi^*(N_{19}\text{-}C_{23})$, $\pi(N_{19}\text{-}C_{23})\rightarrow\pi^*(C_{16}\text{-}C_{17})$ and $\pi(C_{14}\text{-}O_{15})\rightarrow\pi^*(C_{16}\text{-}C_{17})$ 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 T_2CNH molecule. The S_1, N_{12} & 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 hyperconjucative E(2) energy of heteroatoms during the inter-molecular interaction leads the molecule towards medicinal and biological applications [28]. The bond $\sigma(C_3\text{-}H_8)$ transfer more energy (23.39 KJ/mol) to $\sigma^*(S_1\text{-}C_2)$ bond on comparing with energy transfer (18.95 KJ/mol) from $\sigma(C_4\text{-}H_7)$ to $\sigma^*(S_1\text{-}C_5)$. Hence the $\nu(S_1\text{-}C_2)$ mode observe at higher frequency 791 cm^{-1} (mode no: 43) than the $\nu(S_1\text{-}C_5)$ mode (718 cm^{-1}/mode no: 44).

HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) analysis is very important parameters for quantum chemistry. The energy values of HOMO (π-donor) and LUMO (π-acceptor) and its energy gap 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 is located over the thiophene and hydrozone moieties. The LUMO is located over pyridine ring. The LUMO transition implies that an ED transfer to pyridine ring via hydrazone linkage. The HOMO and LUMO energies 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 π-π* (or) σ-σ* 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 T_2CNH. 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 (λmax) 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

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

Type	Donor NBO (i)	ED/e	Acceptor NBO (j)	ED/e	$E^{(2)}$ kJ/mol	E(j)-E(i) a.u.	F(i,j) a.u.
π -π*	BD (2) C2 - C3	1.795	BD*(2) C4 - C5	0.309	69.58	0.28	0.06
			BD*(2) C9 - N11	0.209	76.65	0.28	0.06
σ -σ*	BD (1) C3 - H8	1.972	BD*(1) S1 - C2	0.028	23.39	0.73	0.06
			BD*(1) C2 - C3	0.021	7.57	1.12	0.04
			BD*(1) C4 - C5	0.014	8.08	1.11	0.04
π -π*	BD (2) C4 - C5	1.846	BD*(2) C2 - C3	0.351	66.02	0.30	0.06
σ -σ*	BD (1) C4 - H7	1.976	BD*(1) S1 - C5	0.017	18.95	0.75	0.05
			BD*(1) C2 - C3	0.021	8.03	1.12	0.04
			BD*(1) C4 - C5	0.014	5.73	1.12	0.04
π -π*	BD (2) C14 - O15	1.980	BD*(2) C16 - C17	0.335	15.10	0.40	0.04
π -π*	BD (2) C16 - C17	1.633	BD*(2) C14 - O15	0.277	65.98	0.3	0.06
			BD*(2) C18 - C21	0.277	89.54	0.29	0.07
			BD*(2) N19 - C23	0.366	69.71	0.27	0.06
π -π*	BD (2) C18 - C21	1.636	BD*(2) C16 - C17	0.335	74.85	0.28	0.06
			BD*(2) N19 - C23	0.366	122.13	0.27	0.08
π -π*	BD (2) N19 - C23	1.706	BD*(2) C16 - C17	0.335	112.97	0.32	0.08
			BD*(2) C18 - C21	0.277	52.59	0.33	0.06
n -π*	LP (2) S1	1.622	BD*(2) C2 - C3	0.351	87.15	0.27	0.07
			BD*(2) C4 - C5	0.309	91.55	0.26	0.07
n -π*	LP (2) N12	1.667	BD*(2) C9 - N11	0.209	115.14	0.29	0.08
			BD*(2) C14 - O15	0.017	4.44	0.88	0.03
			BD*(2) C14 - O15	0.277	190.41	0.32	0.11
n -σ*	LP (1) O15	1.855	BD*(1) N12 - C14	0.084	118.2	0.67	0.12
			BD*(1) C14 - C16	0.069	80.37	0.66	0.10
n -σ*	LP (1) N19	1.916	BD*(1) C16 - C17	0.033	39.33	0.90	0.08

Table 5 The frontier molecular orbital of T_2CNH.

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 6 The Physico-Chemical properties of T_2CNH.

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

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.

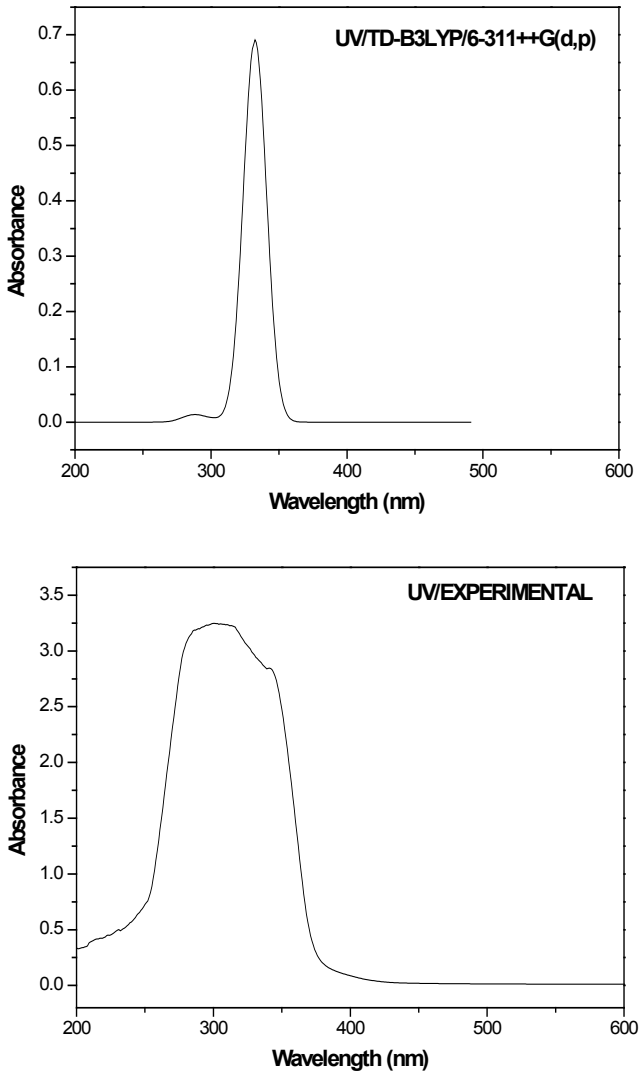


Figure 5 The Theoretical and Experimental UV-Visible spectra of T_2CNH.

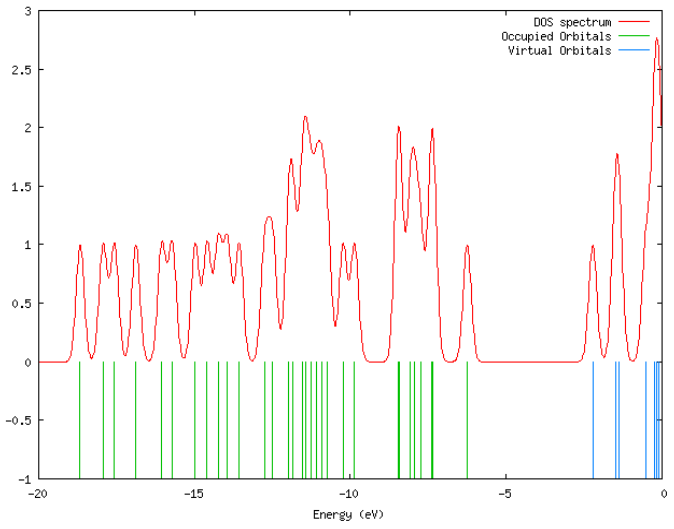


Figure 6 The DOS spectrum of T_2CNH.

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_2CNH, 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 T2CNH 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 T2CNH is shown in **Figure 8.** The C_9/C_3

Table 7 The electronic transition of T2CNH.

Calculated at B3LYP/ 6-311++G(d,p)	Oscillator strength	Calculated Band gap (ev/nm)	Experimental Band gap (nm)	Type
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 -> 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		

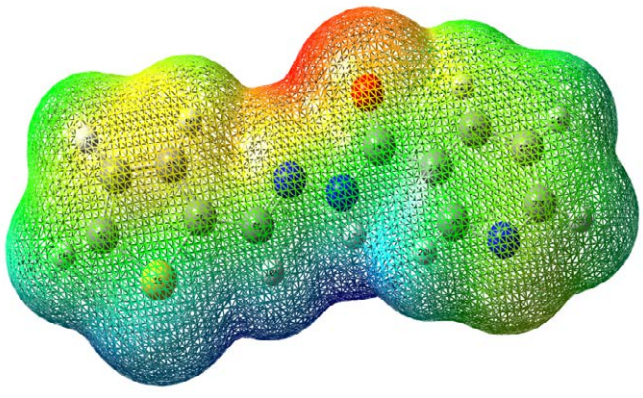


Figure 7 Molecular electrostatic potential map of T_2CNH.

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 are listed in **Table 9**. The thermodynamic parameters viz, entropy (S^0_m), enthalpy (ΔH^0_m) and heat capacity at constant pressure ($C^0_{p,m}$) for T2CNH was 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 × 10^{-5} T^2 (R^2=0.99929)

S^0_m=1.35549+0.00572T+5.0560 × 10^{-5} T^2 (R^2=0.99997)

ΔH^0_m=3.15466+0.01332T+1.1767 × 10^{-5} T^2 (R^2=0.99944)

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

Table 8 The Mulliken atomic charges of T_2CNH.

Atoms	Charges	Atoms	Charges	Atoms	Charges
S1	-0.6516	H10	0.1263	N19	-0.0124
C2	0.2759	N11	0.1794	H20	0.1758
C3	1.9917	N12	-0.0550	C21	-0.0964
C4	-1.2036	H13	0.2477	H22	0.2280
C5	0.4451	C14	-0.7857	C23	-0.3517
H6	0.2687	O15	-0.2925	H24	0.1897
H7	0.1582	C16	0.9920	H25	0.1903
H8	0.2452	C17	-0.5899		
C9	-1.7721	C18	0.0967		

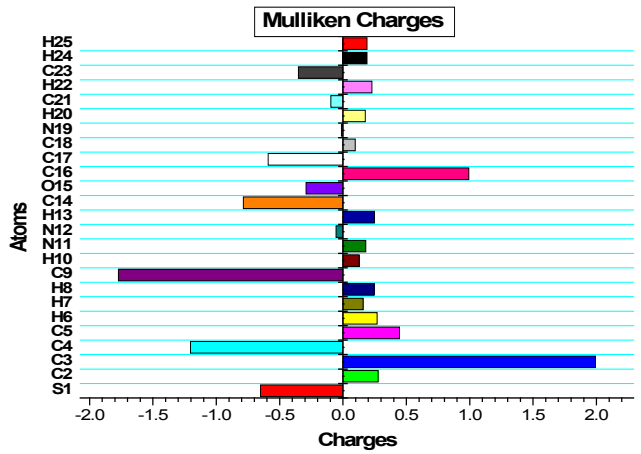


Figure 8 The Mulliken atomic charges of T_2CNH.

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_2CNH.

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

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_2CNH. The calculated bond parameters are good agreement with the related single crystal X-ray diffraction (XRD) data. In T_2CNH, the thiophene and hydrazone moieties are co-planar, which shows a good conjuction between p-orbitals of all atoms of thiophene and hydrazone moieties. The vibrational

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

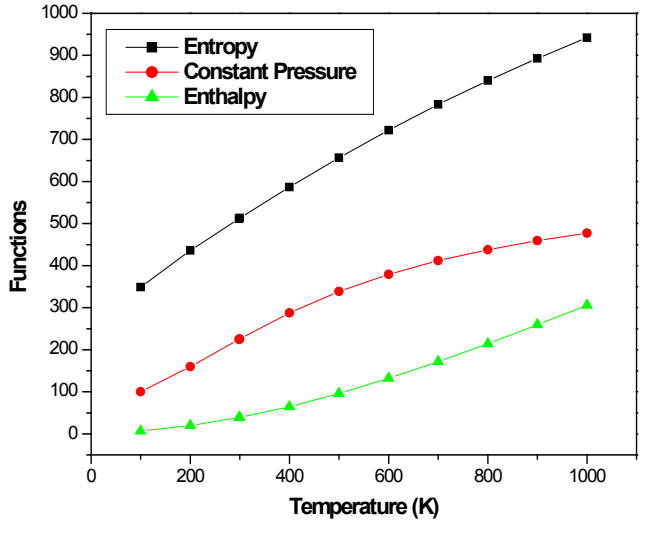


Figure 9 The thermodynamic properties of T2CNH at different temperatures.

data of T2CNH are well supported by the harmonic and related literature values. The β0 value of T2CNH molecule is found to be 1.5861×10^{-30} esu, which is four time greater thatn 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_2CNH 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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