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FT-Raman, FT-IR spectral and DFT studies on (*E*)-1-4-nitrobenzylidenethiocarbonohydrazide

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ABSTRACT

Quantum mechanical calculation of optimized parameters, vibrational wavenumbers and energies of (*E*)-1-4-nitrobenzylidenethiocarbonohydrazide ((*E*)-1-4-NBTCH) was carried out using Hatree Fock (HF) with 6-31G(d,p), 6-311G(d,p) basis sets and density functional theory (DFT) with 6-31G(d,p) basis set. The optimized geometrical parameters obtained by HF and DFT are in better agreement with analogues single XRD data. The vibrational wavenumbers were calculated and the complete assignments were performed on the basis of total energy distribution (TED), calculated with scaled quantum mechanical (SQM) method. The electrical dipole moment (μ) and first hyperpolarizability (β_0) values have been computed using *ab initio* and DFT quantum mechanical calculation. The calculated results (β_0) show that the title molecule might have nonlinear optical (NLO) behaviour. The total energy, dipole moment and rotational constant are reported for the title molecule. The HOMO–LUMO energies were calculated and natural bonding orbital (NBO) analysis has also been carried out.

1. Introduction

Recently, thiosemicarbazone derivatives have been investigated and shown to be successfully applicable in biological system, thiosemicarbazones show very interesting and important biological activity in pharmaceutical and industrial aspects as antibacterial [1], antimalarial [2], antioxidant activity [3], anticancer [4], and anticonvulsant [5]. Furthermore, 4-diethylamino-salicylaldehyde-4-phenylthiosemicarbazone acts as a antitumor which suggested the possibility of DNA binding by intercalation. Physicochemical and structural properties of thiosemicarbazone derivatives clearly display stronger antiproliferative activity on tumor cell [6].

To our knowledge, theoretical study of complete FT-IR and FT-Raman of (*E*)-1-4-NBTCH have not yet been reported so for. In this study, HF and DFT levels of theories were utilized to determine the optimized geometry, vibrational wave numbers in its ground state, dipole moment (μ), polarizability (α), hyperpolarizability (β), chemical potential, hardness (η), electrophilicity (ω) and the HOMO–LUMO energies. NBO analysis of (*E*)-1-4-NBTCH was performed in the same level of theories to determine the second order perturbation energy in terms of delocalization energy $E^{(2)}$.

2. Experimental details

(*E*)-1-4-Nitrobenzylidenethiocarbonohydrazide was prepared from *p*-nitrobenzaldehyde and thiocarbohydrazide by simple condensation method (1:1) and microanalysis data consistent with reported value [7]. The FT-IR spectrum of (*E*)-1-4-NBTCH was recorded in the range of 4000–400 cm^{-1} on Nexus 670 spectrophotometer using KBr pellet technique with spectral resolution of 2.0 cm^{-1}. The FT-Raman spectrum of (*E*)-1-4-NBTCH has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on a Thermo Electron corporation model Nexus 670 spectrophotometer equipped with FT-Raman module accessory. The spectral measurements were carried out at Central Electro Chemical Research Institute, Karaikudi, Tamilnadu and India.

3. Computational details

Ab inito computations were performed at HF/6-31G(d,p), 6-311G(d,p) basis sets and DFT/B3LYP/6-31G(d,p) basis set using Gaussian 03 program package [8]. The optimum geometry is

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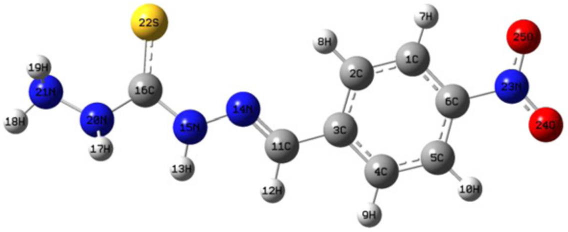

Fig. 1. Optimized molecular structure of (*E*)-1-4-NBTCH.

determined by minimizing the energy with respect to all geometry parameters without imposing molecular symmetry constraints. Among the two computational methods, the DFT/B3LYP method with 6-31G(d,p) basis set takes considerable computational time which comes out best for the calculation of the geometries and wave number than the HF method. The time consideration is due to the inclusion of electron correlation in DFT calculation.

HF and DFT hybrid B3LYP functional methods tend to overestimate the fundamental modes. Therefore, scaling factor has to use for obtaining a considerably better agreement with experimental data [9]. Thus, the scaling factors 0.8992, 0.9051 and 0.9550 [10] have been uniformly applied to the HF and DFT-B3LYP methods, respectively.

3.1. Prediction of Raman intensity

It should be noted that Gaussian 03 package does not calculate the Raman intensities. The Raman activities were transformed into Raman intensities using Rain program [11] by the expression:

$$I_i = 10^{-12} \times (\nu_0 - \nu_i)^4 \times \frac{1}{\nu_i} \times \mathrm{RA}_i \qquad (1)$$

where I_i is the Raman intensity, RA_i is the Raman scattering activities, ν_i is the wave number of the normal modes and ν_0 denotes the wave number of the excitation laser [12].

4. Results and discussion

4.1. Molecular geometry

The title molecule (*E*)-1-4-NBTCH contains *p*-nitrophenyl ring bonded through imino linkage to thiocarbohydrazide. The atom numbering scheme for the title molecule is shown in Fig. 1. The bond distances, bond angles and dihedral angles for the title molecule are computed at HF/6-31G(d,p), HF/6-311G(d,p) and DFT-B3LYP/6-31G(d,p) levels. Since, the crystal structure data of the title compound is not available till now, the optimized geometrical parameters are compared with other similar systems like (*E*)-4-(benzylox)benzaldehyde thiosemicarbazone ((*E*)-4-BTC) [13] and 4-amino-3-methyl-1,2,4-triazole-5-thione derivative of *p*-nitrophenylaldehyde [14] for which experimental crystal data have been solved (Table 1).

The C–C bond distances C1–C2: 1.378, C1–C6: 1.386, C2–C3: 1.395, C3–C4: 1.389, C4–C5: 1.383 and C5–C6: 1.379 are calculated using HF/6-31G(d,p) basis set are in line with literature values [15,16], while the predicted bond length for C3–C11 linkage is negatively deviated (0.004 Å: HF/6-311G(d,p)) from the literature (1.466). Literature value for C–H bond distance is 0.930 Å. The predicted C–H bond distances around 1.09 Å and 1.08 Å HF/6-311G(d,p) are belongs to C11–H12 and all the C–H bonds in the phenyl ring of the title compound. The calculated bond lengths C16=S22, N14–N15 and N15–H13, N15–C16 are shortened and elongated, respectively, on comparing with literature values [15,16].

On comparing the bond angles C2–C3–C4: 119.22° and C1–C6–C5: 121.96° (HF/6-311G(d,p)), C1–C6–C5 has higher value. It may be due to the addition of NO_2 group at C6 in the phenyl ring of the title compound. Similarly, the bond angles C11–N15–N14 and C16–N14–N15 are different due to the addition of sulphur with C16. The predicted bond angles of C1–C2–H8 and C3–C2–H8 are differing by 1° from each other. This may be due to a possible attraction on H8 from N14 atom. In the present work, the optimized bond parameters (bond length, bond angle) calculated by HF/6-31G(d,p) method are much closer to literature values [15,16].

4.2. Vibrational assignments

The molecule (*E*)-1-4-NBTCH belongs to C_1 point group symmetry, has 25 atoms and hence one can have 69 fundamental vibrations, which are active in both IR and Raman. The vibrational assignments are made on the basis of TED with the help of SQM calculation using the same basis set.

The harmonic vibrational frequencies calculated for (*E*)-1-4-NBTCH at HF/6-31G(d,p), 6-311G(d,p) and DFT-B3LYP/6-31G(d,p) levels along with observed FT-IR and FT-Raman frequencies are given in Table 2. Comparison of the frequencies calculated by HF and B3LYP methods with experimental values reveal the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusions of electron correlation in DFT to certain extend make the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations through basis set sensitive are only marginal as calculated in the DFT values using 6-31G(d,p). Anyway notwithstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. The calculated frequencies were scaled by factors 0.8992, 0.9051 and 0.9550 for HF and DFT computation, respectively [10]. These values minimize the root mean square difference between calculated and experimental frequencies for bands with definite identification. The descriptions concerning the assignment have also been indicated in Table 2. The combined experimental and theoretical spectra of (*E*)-1-4-NBTCH are shown in Figs. 2 and 3.

4.2.1. C–H stretching vibrations

The aromatic C–H stretching is normally found in the region between 3100 and 3000 cm^{-1} [15]. In the present study, the aromatic C–H stretching vibrations are assigned in the region 3101–3046 cm^{-1} (B3LYP) (mode nos: 62–65) which are in good agreement with the literature values [16,17] and also find support from observed FT-IR: 3101 cm^{-1} band.

In aromatic compounds, the C–H in-plane bending frequencies appear in the range 1000–1300 cm^{-1} and C–H out-plane bending vibrations are in the range 750–1000 cm^{-1} [18,19]. From the above literature, the harmonic vibrations in the range 1077–1300 cm^{-1}/B3LYP (mode nos: 40–42, 45, 47 and 48) and 962–813 cm^{-1}/B3LYP mode nos: 37–35, 33, and 30 are assigned to C–H in-plane and C–H out-of-plane bending, respectively. The observed FT-IR bands 1092 and 938, 850 cm^{-1} are attributed to C–H in-plane and out-of-plane bending, respectively, and their corresponding Raman counterparts are 1294, 1216, 1087 and 937 cm^{-1}. These assignments are found to be satisfactorily in agreement with theoretical and the already reported values [20,21]. Among the two computational methods DFT/B3LYP show excellent agreement with literature values. Abraham et al. [22] assigned the aliphatic C–H stretching vibration at 2999 cm^{-1}. The predicted C–H stretching mode (2903 cm^{-1}/B3LYP/mode no: 61) is moderately close to the literature value.

Table 1
Optimized bond length, bond angle and dihedral angle of (*E*)-1-4-NBTCH.

Parameters	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	HF/6-311G(d,p)	XRD[a]
Bond length (Å)				
C1–C2	1.378	1.377	1.387	1.377
C1–C6	1.386	1.385	1.397	1.384
C1–H7	1.071	1.071	1.083	0.930
C2–C3	1.395	1.394	1.409	1.375
C2–H8	1.073	1.073	1.084	0.930
C3–C4	1.389	1.388	1.406	1.388
C3–C11	1.476	1.476	1.462	1.466
C4–C5	1.383	1.383	1.390	1.377
C4–H9	1.076	1.075	1.086	0.930
C5–C6	1.380	1.378	1.393	1.371
C5–H10	1.071	1.071	1.082	0.930
C11–H12	1.085	1.086	1.099	0.930
C11=N14	1.254	1.251	1.286	1.274
N15–H13	0.999	0.999	1.020	0.860
N14–N15	1.346	1.345	1.344	1.385
N15–C16	1.369	1.369	1.391	1.342
C16=S22	1.646	1.643	1.649	1.693
Bond angle (°)				
C2–C1–C6	118.91	118.93	119.00	119.8
C2–C1–H7	118.91	121.17	121.67	120.1
C6–C1–H7	119.92	119.91	119.34	120.1
C1–C2–C3	120.15	120.15	120.41	121.1
C1–C2–H8	120.44	120.42	120.67	119.5
C3–C2–H8	119.42	119.42	118.92	119.5
C2–C3–C4	119.70	119.69	119.22	118.8
C2–C3–C11	121.20	121.21	121.51	121.9
C4–C3–C11	119.10	119.10	119.27	119.3
C3–C4–C5	120.69	120.68	120.85	120.4
C3–C4–H9	120.10	120.12	119.67	119.8
C5–C4–H9	119.21	119.20	119.48	119.8
C4–C5–C6	118.42	118.43	118.57	120.4
C4–C5–H10	121.43	121.43	121.94	119.8
C6–C5–H10	120.15	120.15	119.49	119.8
C1–C6–C5	122.13	122.12	121.96	119.7
C1–C6–N23	119.03	119.03	119.12	118.9
C3–C11–H12	116.86	116.78	117.09	120.0
C3–C11–N14	120.93	121.06	121.04	120.0
H13–N15–N14	118.26	118.21	119.24	120.8
H13–N15–C16	117.73	117.32	117.54	120.8
C16–N15–N14	121.78	121.77	122.23	118.4
N15–C16=S22	125.11	125.23	125.40	119.90
C6–N23–O24	117.66	117.55	117.70	118.1
C6–N23–O25	117.68	117.56	117.70	118.8
O24–N23–O25	124.67	124.90	124.60	123.1
Dihedral angle (°)				
C6–C1–C2–C3	0.02	0.01	−0.01	0.40
C2–C1–C6–C5	0.09	0.09	0.10	−0.20
C1–C2–C3–C4	−0.14	−0.13	−0.11	−0.40
C1–C2–C3–C11	179.99	179.99	−179.95	−179.5
C2–C3–C4–C5	0.16	0.15	0.14	0.20
C11–C3–C4–C5	−179.97	−179.97	−179.98	−179.50
C2–C3–C11–H12	177.84	178.00	178.51	174.50
C4–C3–C11–N14	177.94	178.06	178.65	174.5
C3–C4–C5–C6	−0.05	−0.05	−0.04	0.00
C4–C5–C6–C1	−0.07	−0.07	−0.08	0.00
C3–C11–N14–N15	−179.09	−179.02	−178.95	−175.60
C11–N14–N15–C16	−169.14	−168.22	−171.18	−173.60

[a] Refs [13,14].

4.2.2. *C–C vibrations*

There are six equivalent C–C bonds in benzene ring and one C–C bond outside the ring consequently there will be seven C–C stretching. In general, bands around 1400–1650 cm^{-1} are assigned to skeletal stretching bands of benzene and its derivatives [19]. In the present work, C–C stretching vibration modes coupled with $\nu(\text{NO}_2)$ and ν (C=N) are assigned in the region 1587–1462 cm^{-1} B3LYP/(mode nos: 54, 56–58). In the Raman spectrum their corresponding modes are assigned at 1595 and 1578 cm^{-1}. The ring breathing mode appears as weak band near 1000 cm^{-1} for IR vibration [23]. The theoretically computed ring breathing is assigned at 983 cm^{-1} (B3LYP/mode no: 38), while HF values are 1019 cm^{-1}/6-31G(d,p) and 1018 cm^{-1}/6-311G(d,p). The FT-IR bands at 665 and 608 cm^{-1} are assigned to deformation of phenyl ring [24]. The theoretically computed phenyl ring deformation vibrations are observed at 657, 615 cm^{-1} (B3LYP/mode no: 25, 24), and 661, 622 cm^{-1} (HF/6-31G(d,p)) and 666, 624 cm^{-1} (HF/6-311G(d,p)).

4.2.3. *C=N and C–N stretching vibrations*

Identification of C–N vibration is a difficult task since the mixing of vibrations is possible in this region. However, with the help of molecular simulation program (GaussView 3.0) the C–N vibrations are described and assigned in the present work. The C=N

Table 2
Vibrational wave numbers obtained for (*E*)-1-4-NBTCH [harmonic frequency (cm^{-1}), IR, Raman intensities (km/mol), reduced masses (amu) and force constants (mdyn Å^{-1})].

Mode no	Observed		Scaled frequencies (cm^{-1})			Intensity				Vibrational assignment TED ≥ 10%
	FT-IR	FT-Raman	DFT/B3LYP/6-31G(d,p)	HF/6-31G(d,p)	HF/6-311G(d,p)	IR$_c$	RS$_c$	Reduced Mass	Force constant	
1			31	27	26	0.64	5.34	7.36	0.00	$\Gamma_{N14C11C3C2}(15)+\Gamma_{N14C11C3C4}(20)+\Gamma_{C16N15N14C11}(19)$
2			33	33	34	0.45	1.69	6.78	0.00	$\Gamma_{N15N14C11C3}(17)+\Gamma_{N20C16N15N14}(23)+\Gamma_{S22C16N15N14}(16)$
3			45	45	45	0.39	5.49	8.32	0.01	$\Gamma_{N14C11C3}(20)+\Gamma_{15N14C11}(23)+\Gamma_{C16N15N14}(13)$
4			63	53	47	0.03	0.78	6.65	0.02	$\Gamma_{O24N23C6C1}(21)+\Gamma_{O24N23C6C5}(21)+\Gamma_{O25N23C6C1}(21)+\Gamma_{O25N23C6C5}(22)$
5			81	80	80	0.59	0.65	7.06	0.03	$\Gamma_{C16N15N14C11}(21)+\Gamma_{N20C16N15N14}(15)$
6			128	134	138	11.18	14.67	1.34	0.01	$\Gamma_{H17N20C16N15}(11)+\Gamma_{H18N21N20C16}(23)$ $\Gamma_{H19N21N20C16}(24)+\Gamma_{H17N20C16S22}(13)$
7			138	144	144	0.10	3.58	5.93	0.07	$\delta_{C11C3C2}(11)+\delta_{C16N15N14}(11)+\Gamma_{N21N20C16N15}(13)$
8			161	159	161	0.61	1.51	4.27	0.07	$\Gamma_{N14C11C3C4}(13)$
9			190	188	190	0.91	0.52	6.07	0.14	$\delta_{NCC}(12)$
10			209	204	207	1.49	0.74	3.81	0.11	$\Gamma_{N15N14C11}(12)$
11			233	233	235	3.47	0.65	3.81	0.13	$\Gamma_{H12C11C3C2}(16)+\Gamma_{N15N14C11C3}(13)$
12			255	263	263	0.77	0.62	7.29	0.31	$\delta_{S22C16N15}(12)+\delta_{N23C6C1}(21)+\delta_{N23C6C5}(20)$
13			286	288	291	1.58	1.70	3.57	0.19	$\delta_{N21N20C16}(18)+\delta_{N20C16S22}(15)$
14			335	351	353	0.09	0.54	5.55	0.40	$\Gamma_{N15N14C11C3}(18)$
15			383	389	389	2.70	1.53	5.50	0.52	$\delta_{C4C3C11}(12)+\delta_{N15N14C11}(15)+\delta_{S22C16N15}(14)$
16			399	409	410	0.76	1.16	6.23	0.64	$\nu_{N23C6}(20)$
17	409		403	413	414	0.09	0.09	3.10	0.33	$\Gamma_{C3C2C1C6}(18)+\Gamma_{C6C5C4C3}(18)$
18			458	425	422	27.66	4.57	1.77	0.24	$\Gamma_{H18N21N20H17}(16)+\Gamma_{H19N21N20H1}7(13)+\Gamma_{H17N20C16S22}(15)$
19			493	464	471	4.57	7.15	2.00	0.31	$\Gamma_{H13N15N14C11}(17)+\Gamma_{N20C16N15H13}(13)$
20	503		500	510	512	8.88	6.48	2.54	0.41	$\Gamma_{H13N15N14C11}(16)$
21			511	517	521	4.50	2.11	3.49	0.59	$\delta_{O24N23C6}(24)+\delta_{O25N23C6}(25)$
22			557	561	564	2.88	2.59	5.07	1.02	$\delta_{NNC}(12)$
23			563	604	603	2.58	0.50	4.36	0.89	$\delta_{SCN}(14)$
24			615	622	624	0.32	0.63	7.00	1.71	$\delta_{C3C2C1}(11)+\delta_{C5C4C3}(15)+\delta_{C2C1C6}(13)+\delta_{C6C5C4}(13)$
27	689		684	699	702	12.92	1.68	2.66	0.80	$\Gamma_{H19N21N20H17}(10)$
28			726	735	740	2.43	0.33	5.14	1.75	$\Gamma_{O24N23C6C5}(24)+\Gamma_{O25N23C6C1}(24)$
29			733	770	762	7.31	1.31	7.01	2.43	$\nu_{S22C16}(34)$
30			813	820	843	0.96	0.24	1.31	0.56	$\Gamma_{H9C4C3C2}(13)+\Gamma_{C6C5C4H9}(16)+\Gamma_{H10C5C4C3}(12)+\Gamma_{H9C4C3C11}(16)+\Gamma_{N23C6C5H10}(12)$
31			814	854	855	12.06	1.18	3.15	1.35	$\delta_{O24N23O25}(17)$
32			827	857	868	14.36	0.55	2.79	1.23	$\delta_{O24N23O25}(14)$
33	850		839	876	877	2.80	0.14	1.54	0.70	$\Gamma_{C3C2C1H7}(14)+\Gamma_{H8C2C1C6}(15)+\Gamma_{C11C3C2H8}(14)+\Gamma_{N23C6C1H7}(15)$
34			867	879	884	3.40	0.75	3.91	1.90	$\nu_{C3C2}(19)+\delta_{N15N14C11}(13)$
35			910	970	973	3.70	0.42	1.54	0.83	$\Gamma_{H12C11C3C2}(13)+\Gamma_{H12C11C3C4}(22)+\Gamma_{N15N14C11H12}(42)$
36	938	937	940	997	996	0.01	0.23	1.34	0.77	$\Gamma_{H10C5C4H9}(39)+\Gamma_{N23C6C5H10}(12)$
37			962	999	1000	0.01	0.16	1.31	0.78	$\Gamma_{H8C2C1H7}(42)+\Gamma_{C11C3C2H8}(11)+\Gamma_{N23C6C1H7}(10)$
38			983	1019	1018	0.20	1.91	2.77	1.73	$\nu_{CC}(33)+\delta_{CCC}(34)+\delta_{CCH}(33)$
39			1057	1074	1072	5.82	6.13	4.21	3.04	$\nu_{N15N14}(22)+\nu_{N20C16}(12)+\nu_{N21N20}(34)$
40			1077	1077	1075	18.50	17.48	2.80	2.10	$\nu_{C6C1}(15)+\nu_{C6C5}(13)+\nu_{N23C6}(23)+\delta_{H10C5C4}(12)$
41	1092	1087	1083	1114	1114	2.53	0.75	1.35	1.02	$\nu_{C5C4}(14)+\nu_{C2C1H7}(14)+\delta_{H10C5C4}(10)$
42			1149	1167	1167	5.62	10.11	1.31	1.12	$\delta_{H8C2C1}(12)+\delta_{H9C4C3}(12)+\delta_{C5C4H9}(14)$
43			1158	1173	1172	58.11	23.69	3.11	2.70	$\nu_{N15N14}(33)$
44			1193	1204	1201	50.97	1.08	2.74	2.52	$\nu_{C16N15}(23)+\nu_{N21N20}(18)$
45		1216	1212	1223	1225	38.33	7.65	2.27	2.15	$\nu_{C11C3}(20)+\nu_{N15N14}(15)+\delta_{H12C11N14}(10)$
46	1247		1257	1242	1244	6.26	0.90	1.61	1.64	$\delta_{N20C16}(11)+\delta_{H18N21N20}(16)+\delta_{H19N21N20}(22)$
47			1268	1285	1291	1.14	2.66	1.35	1.40	$\delta_{H8C2C1}(10)+\delta_{H18N21N20}(10)+\delta_{H19N21N20}(13)$
48		1294	1300	1300	1304	5.28	1.28	2.04	2.22	$\delta_{H12C11N14}(11)+\delta_{H19N21N20}(11)$
49			1321	1323	1328	19.36	1.18	4.18	4.71	$\nu_{C3C2}(10)+\nu_{C4C3}(11)+\nu_{C6C5}(10)$
50	1339	1337	1330	1377	1378	100.00	47.81	11.73	13.40	$\nu_{O24N23}(36)+\nu_{O25N23}(37)$
51			1355	1412	1411	10.93	0.68	2.30	2.73	$\nu_{N20C16}(15)+\delta_{H12C11N14}(16)$
52			1387	1474	1477	2.01	3.74	3.07	3.82	$\nu_{C2C1}(18)+\nu_{C5C4}(18)$
55			1486	1550	1553	39.97	0.96	1.92	2.74	$\delta_{H13N15N14}(29)+\delta_{C16N15H13}(25)$

56			1535	1591	1591	21.93	7.58	9.45	14.39	$\nu_{C6C5}(14)+\nu_{O24N23}(21)+\nu_{O25N23}(23)$
57		1578	1573	1627	1626	16.55	100.00	6.00	9.58	$\nu_{C2C1}(17)+\nu_{C5C4}(13)+\nu_{N14C11}(14)$
58		1595	1587	1652	1661	14.82	0.38	8.99	14.64	$\nu_{C6C1}(13)+\nu_{O24N23}(18)+\nu_{O25N23}(21)$
59	1602		1603	1678	1675	9.33	3.50	1.19	1.98	$\delta_{H18N21H19}(46)+\delta_{H18N21N20}(20)+\delta_{H19N21N20}(17)$
60			1608	1721	1718	5.76	25.93	5.30	8.85	$\nu_{N14C11}(50)$
61			2903	2910	2909	9.48	0.31	1.09	5.92	$\nu_{H12C11}(100)$
62			3046	3017	3019	1.67	0.31	1.09	6.54	$\nu_{H9C4}(98)$
63			3080	3053	3053	0.08	0.06	1.09	6.68	$\nu_{H8C2}(93)$
64	3101		3101	3077	3076	0.11	0.28	1.09	6.79	$\nu_{H7C1}(19)+\nu_{H10C5}(79)$
65			3101	3077	3077	0.20	0.46	1.09	6.80	$\nu_{H7C1}(74)+\nu_{H10C5}(19)$
66			3306	3379	3380	0.60	1.31	1.05	7.42	$\nu_{N21H18}(18)+\nu_{N21H19}(80)$
67			3309	3411	3414	1.82	0.86	1.07	7.60	$\nu_{N15H13}(81)+\nu_{N20H17}(17)$
68			3313	3416	3418	5.00	1.49	1.07	7.62	$\nu_{N15H13}(18)+\nu_{N20H17}(82)$
69	3450		3440	3490	3484	0.90	0.59	1.09	8.36	$\nu_{N21H18}(82)+\nu_{N21H19}(18)$

ν, stretching; δ, scissoring, Γ, torsion; s, strong; m, medium; w, weak; v, very. Scale factors: 0.955 (B3LYP), 0.8992 [HF/6-31G(d,p)], 0.9051 [HF/6-311G(d,p)].

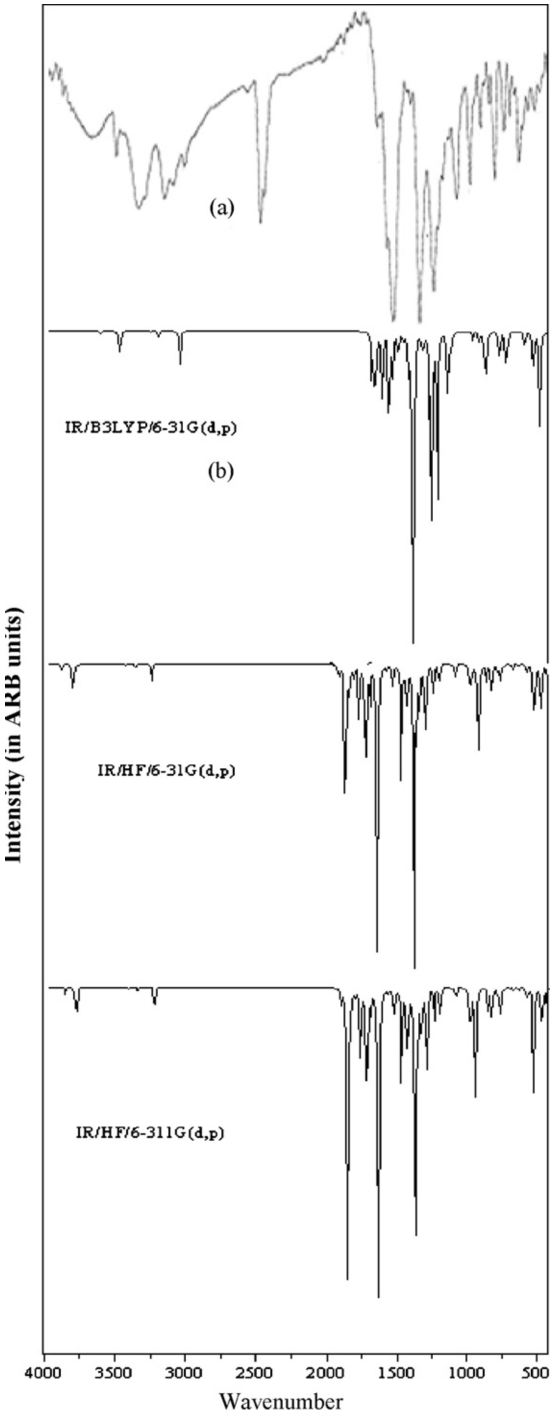

Fig. 2. The experimental (a) and theoretical (b) FT-IR spectra of (*E*)-1-4-NBTCH.

stretching wave number is observed as a strong intense band in IR at 1584 cm^{-1} in the case of benzaldehyde phenylhydrazone [25]. Silverstein and Webstor [26] assigned C=N and C–N stretching vibrations in the range 1471–1689 cm^{-1}, 1266–1382 cm^{-1} and 1020–1250 cm^{-1} (for aromatic amines), respectively. We observed the C=N stretching harmonic vibration modes are 1608 and 1573 cm^{-1} (B3LYP/mode nos: 60, 57) as a mixture of νC=C vibration for (*E*)-1-4-NBTCH and similarly the C–N stretching (harmonic) modes (1355, 1193, 1077 and 1057 cm^{-1}/B3LYP mode nos: 51,44,40 and 39) appear as a mixture of βC–H, νN–N, νC–C and νNO_2(sy) vibrations. Their corresponding experimental Raman band at 1578 cm^{-1} is in agreement with theoretical value.

Table 3a
The *ab inito* and DFT calculated electric dipole moments (Debye) for (*E*)-1-4-NBTCH.

Parameters	HF/6-31G(d,p)	HF/6-311G(d,p)	B3LYP/6-31G(d,p)	Experimental [39]
μ_x	−4.1860	−4.4121	−3.3589	–
μ_y	−5.1232	−5.1610	−4.3113	–
μ_z	2.1040	2.0683	2.1234	–
μ	6.9424	7.0979	5.8634	3.70

4.2.4. NH_2 group vibrations

The molecule under study possesses one –NH_2 group and hence one can expects a symmetric and asymmetric stretching vibration. According to Socrates [27], the frequencies of amino group are around at 3500–3300 cm^{-1} for NH_2 stretching, 1700–1600 cm^{-1} for NH_2 stretching, scissoring and 1150–900 cm^{-1} rocking deformations, respectively. The asymmetric and symmetric stretching modes of NH_2 group are calculated at 3440 and 3306 cm^{-1}, respectively, in (*E*)-1-4-NBTCH by B3LYP/(mode nos: 69, 66) method. Mode no: 69 is in agreement with experimental value of 3450 cm^{-1} in FT-IR. The symmetric NH_2 vibration is missing in both FT-IR and FT-Raman spectra. The harmonic N–H stretching frequencies (N15–H13 and N20–H17) are assigned at 3313 and 3309 cm^{-1} (B3LYP/mode nos: 68, 67). The computed –NH_2 scissoring vibration at 1603 cm^{-1} by B3LYP/mode no: 59 is in good agreement with the expected characteristic value 1600 cm^{-1} [26]. This is also in very good agreement with the recorded 1602 cm^{-1} band in FT-IR spectrum and also correlates well with observed FT-IR band at 1608 cm^{-1} in the case of *p*-aminoacetanilide [28]. The rocking mode of the NH_2 group appears in the range 1000–1100 cm^{-1} [29] with variable IR intensity. The observed bands at 1247 cm^{-1} (FT-IR) and 1294 cm^{-1} (FT-Raman) attributed to the appreciable contribution from the NNH angle bending suggesting its origin due to the rocking mode. For the same mode the corresponding harmonic modes are 1300, 1268 and 1257 cm^{-1} (B3LYP/mode nos: 48–46). The wagging mode of the NH_2 group appears in the range 600–800 cm^{-1} [30]. The observed FT-IR band at 689 cm^{-1} and the calculated bands 684 cm^{-1} (B3LYP/mode nos: 27) are correspond to ωNH_2 mode. Ramalingam et al. [30] assigned the ωNH_2 mode at 671 cm^{-1} (FT-IR) for 5-amino-2-nitrobenzoic acid. Moreover, the calculated band at 128 cm^{-1} (B3LYP/mode no: 6) and is assigned to torsion mode of amino group.

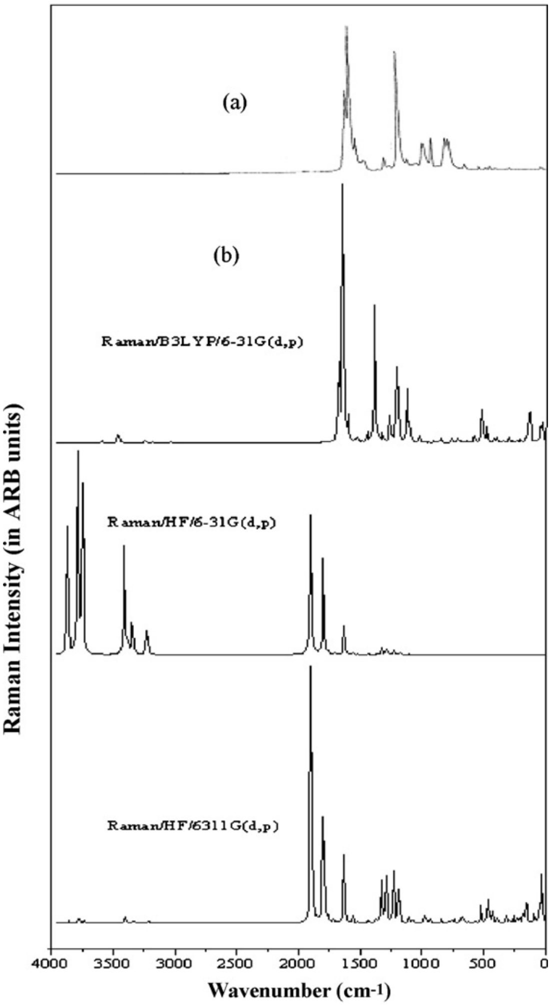

Fig. 3. The experimental (a) and theoretical (b) FT-Raman spectra of (*E*)-1-4-NBTCH.

4.2.5. C=S stretching vibration

According to Silverstein and Webstor [26], spectra of compounds in which C=S group is attached to an N atom show absorption bands in broad region 1563–700 cm^{-1}. In nitrogen containing thiocarbonyl compounds, the assignment of the C=S stretching frequency has been controversial one [31,32]. Mani et al. [33] assigned from PED calculation, the medium intensity band at 988 cm^{-1} in FT-IR to the C=S stretching vibration for phenylisothiocynate. In accordance with above conclusion, the band 733 cm^{-1} calculated by B3LYP method (mode no: 29) has been assigned to C=S stretching vibration. However, there is no other FT-IR and Raman bands were observed.

4.2.6. NO_2 and N–N stretching vibrations

The characteristic group frequencies of nitro group are relatively independent of the rest of the molecule which makes the NO_2 group convenient to identify. The asymmetric and symmetric vibrations of NO_2 generally give rise to bands in the region 1500–1570 cm^{-1} and 1300–1370 cm^{-1} in nitrobenzene and substituted nitrobenzene [34]. Krishnakumar et al. [35] assigned the frequencies at 1489 and 1354 cm^{-1} to ν_{asy} NO_2 and ν_{sy} NO_2 vibrations, respectively. In accordance with above conclusion the harmonic band at 1535 and 1330 cm^{-1}/(1339: FB3LYP/mode nos: 56, 50) corresponds to NO_2 asymmetric and symmetric stretching vibrations, respectively. The theoretical scaled mode number 50 is correlated with the experimental observations (1339 cm^{-1}: FT-IR/1337 cm^{-1} Raman), while the HF values are positively deviated.

The deformation vibration of NO_2 group (rocking, wagging and twisting) contributes to several normal modes in the low frequency region [36,37]. It follows from Table 2 that the harmonic band at 814 cm^{-1} by B3LYP method (mode no: 31) assigned to NO_2 scissoring mode of (*E*)-1-4-NBTCH. The bands at 726 cm^{-1} (mode no: 28) and 511 cm^{-1} (mode no: 21) in B3LYP method have been designated to wagging and rocking modes, respectively, for the nitro group. It should be emphasized that the wave number calculated by both HF/B3LYP (mode no: 4) method at 53/63 cm^{-1} for NO_2 torsion mode is in agreement with the assignment proposed by Ramalingam et al. [30]. In this study, the calculated frequencies 1158 and 1057 cm^{-1} B3LYP/(mode nos: 43 and 39) are assigned to N–N stretching vibrations.

Table 3b
The average polarizability for (*E*)-1-4-NBTCH (α_{tot} ($\times 10^{-30}$) esu).

Parameters	HF/6-31G(d,p)	HF/6-311G(d,p)	B3LYP/6-31G(d,p)
α_{xx}	−118.59	−119.16	−111.43
α_{xy}	0.28	0.55	0.59
α_{yy}	−99.00	−99.97	−97.31
α_{xz}	−7.69	−7.48	−8.65
α_{yz}	8.78	9.10	7.30
α_{zz}	−97.71	−98.69	−96.36
α_0	−26.04	−26.50	−27.41
α_{tot}	207.35	206.40	193.56

4.3. NLO properties

The centrosymmetric thiourea molecule, when substituted with different substituents converted to noncentro-symmetric compounds, which has nonlinear optical properties [38]. The donor and acceptor were required in each side of the conjugated molecules in order to create asymmetric system and increase polarizability [39]. In the present study, the thiocarbanohydrazide is substituted to form a new organic nonlinear optical material. The electric dipole moment and first hyperpolarizability of (*E*)-1-4-NBTCH molecular system was investigated by HF and DFT methods using Gaussian 03 program. From Table 3a, the electric dipole moment μ of (*E*)-1-4-NBTCH is found to be greater than thiourea [40]. The second-order polarizability (β) is shown in Table 3b. It is necessary macroscopic materials having strong nonlinear optical properties that to possess microscope molecules have large hyperpolarizability value [41] (Table 3c). Title molecule has large β value than thiourea [40] and hence that the substituted thiourea is a good nonlinear optical material.

4.4. NBO analysis

Natural bond orbital (NBO) analysis provides an efficient method for studying intra- and intermolecular bonding and interaction among the bonds and also provides a convenient for investigating charge transfer or conjugative interaction in the molecular systems. Some electron donor orbital's, acceptor orbital's and the interacting stabilization energy resulted from the second-order micro disturbance theory are reported [42,43]. The larger $E^{(2)}$ value shows that the more intensive in the interaction between electron donors and electron acceptors i.e., the more donating tendency from the electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbital's and formally correspond to a stabilizing donor–acceptor interaction [44]. The second order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO basis [45]. For each donor (i) and acceptor (j) the stabilization energy $E^{(2)}$ associated with the delocalization $i \rightarrow j$ estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \tag{2}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and $F(i,j)$ is the off diagonal NBO Fock matrix element. In the present investigation, transferring of charge from bond to bond has been studied. The maximum charge delocalization occurs from the lone pairs of atom.

The molecule (*E*)-1-4-NBTCH contain lone pairs oxygen, nitrogen and sulphur atoms in which oxygen, nitrogen and sulphur transfer maximum energy: 162.03, 43.30 and 13.62 kcal/mol, respectively. The intramolecular hyper conjugative interactions are formed by the orbital overlapping between π(C–C) and π^*(C–C) bonding orbital's, which results in the intermolecular charge transfer causing stabilization of the system. These interactions are observed as an increase in electron density in C–C anti-bonding orbital, which weaken the respective bonds. In the present work, the C1–C6 bonding orbital interacts with C2–C3 and C4–C5 anti-bonding orbital lead to give stabilization energy 21.03 and 19.50 kcal/mol, respectively. Similarly, the C2–C3 bonding orbital interacts with C1–C6 and C4–C5 anti-bonding orbital lead to gives stabilization energy of 19.51 and 21.21 kcal/mol, respectively. The C4–C5 bonding orbital interacts with C1–C6 and C2–C3 anti-bonding orbital lead to give stabilization energy 21.37 and 19.69 kcal/mol, respectively. Electron density and delocalization energy for (*E*)-1-4-NBTCH is given in Table 4.

4.5. HOMO–LUMO analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) are the two most important molecular orbitals. The HOMO–LUMO energies were also calculated and the values are listed in Table 5a. The energy gap (ΔE) between HOMO and LUMO energies for the (*E*)-1-4-NBTCH are also given in Table 5a. The energy gap (ΔE) calculated by HF method is less than that of the DFT-B3LYP method. The plot of HOMO–LUMO energies reveal that the HOMO orbitals are mainly derived from 3p orbitals of sulphur and 2p orbitals of nitrogen atoms present in the thiourea moiety. LUMO orbitals are localized on the orbitals of the phenyl ring and 2p orbitals of nitrogen, oxygen and carbon present in the phenyl substitution.

At the HF level, Koopmans theorem suggests that the energy of HOMO is good approximation to the negative experimental ionization potential (IP) [46]. Similarly, Zhou and Parr [47] suggest that the electron affinity for an N-electron system is equal to the negative of the LUMO energy and it is a measure of susceptibility of molecule towards attack by nucleophiles. The dipole moment is the most obvious quantity to describe the polarity of a molecule. Electro-negativity is defined as the negative of the partial derivative

Table 3c
Calculated all β components and β_{tot} ($\times 10^{-30}$) value of (*E*)-1-4-NBTCH.

Parameters	HF/6-31G(d,p)	HF/6-311G(d,p)	B3LYP/6-31G(d,p)	Experimental [40]
β_{xxx}	−366.34	−374.37	−306.07	–
β_{yyy}	−15.85	−16.72	−0.21	–
β_{zzz}	4.66	4.25	4.05	-
β_{xyy}	−4.44	−5.40	−2.04	–
β_{xxy}	−21.36	−23.06	−16.39	–
β_{xxz}	68.37	65.48	66.01	–
β_{xzz}	25.28	25.21	24.75	–
c_{yzz}	−0.30	−0.56	0.67	–
β_{yyz}	0.16	0.25	−0.75	–
β_{xyz}	22.34	23.09	20.42	–
β_{tot}	355.15	363.65	293.16	0.80

Table 4
Second order perturbation theory analysis of Fock matrix[b] in NBO basis for (*E*)-1-4-NBTCH.

Donor (*i*)	ED/e	Acceptor (*j*)	ED/e	$E^{(2)}$ (kcal/mol)[a]
σC1–C2	1.975	σ*C6–O23	0.012	4.28
πC1–C6	1.971	π*C2–C3	0.024	21.03
πC1–C6		π*C4–C5	0.013	19.50
σC1–H7	1.980	σ*C5–C6	0.021	4.10
σC2–C3	1.980	π*C1–C6	0.311	19.51
πC2–C3		π*C4–C5	0.013	21.21
σC2–H8	1.971	σ*C3–C4	0.024	4.23
σC4–C5	1.973	σ*C6–O23	0.012	4.21
πC4–C5	1.980	π*C1–C6	0.311	21.37
πC4–C5		π*C2–C3	0.024	19.69
σC4–H9	1.971	σ*C2–C3	0.012	4.13
σC5–H10	1.979	σ*C1–C6	0.013	4.05
σC11–N14	1.976	π*C11–N14	0.028	4.07
πC16–S22	1.965	σ*H13–N15	0.159	4.86
LPN14	1.913	C11–H12	0.035	10.78
		H13–N15	0.044	9.38
LP(1)N15	1.664	C11–N14	0.008	31.21
		C16–S22	0.367	43.30
LP(1)N20	1.768	C16–S22	0.092	9.46
		C16–S22	0.367	17.22
		H19–N21	0.017	5.71
LP(1)N21	1.960	H17–N20	0.035	8.07
LP(1)S22	1.986	N15–C16	0.074	3.38
		C16–N20	0.071	3.57
LP(2)S22	1.870	N15–C16	0.074	13.62
		C16–N20	0.071	12.63
LP(1)O24	1.981	C6–N23	0.103	4.33
		C6–H23	0.103	12.69
		N23–O25	0.057	19.19
LP(3)O24	1.449	N23–O25	0.629	162.03
LP(1)O25	1.981	C6–N23	0.103	4.33
LP(2)O25	1.898	C6–N23	0.103	12.54
		N23–O24	0.057	19.28

[a] $E^{(2)}$ means energy of hyperconjucative interactions (stabilization energy difference between donor and acceptor *i* and *j* NBO orbital).

[b] *F*(*i*,*j*) is the Fock matrix element between *i* and *j* NBO orbital.

of energy *E* of a molecular system with respect to the number of electrons *N* with a constant external potential *V*(*r*) [48].

$$\mu = -\chi = -\left(\frac{\delta E}{\delta N}\right) V(r) \tag{3}$$

The quadrate relationship between *E* and *N* were reported by Ickowski and Margrave [48] in a finite difference approximation, Eq. (4) can be written as:

$$\chi = -\mu = \frac{I + A}{2} \tag{4}$$

$$\chi_{\text{Koopmans}} = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}$$

A new DFT concept called the electrophilicity index (ω) proposed by Parr et al. [49] in the terms of the two global activity indices, μ and η

$$\omega = \frac{\mu^2}{2\eta} \tag{5}$$

Table 5a
HOMO–LUMO energy calculated by HF/6-31G(d,p), HF/6-311G(d,p) and B3LYP methods for (*E*)-1-4-NBTCH.

Methods	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	HF/6-311G(d,p)
E_{HOMO} (E_{H})	−0.21065	−0.31976	−0.32415
E_{LUMO} (E_{L})	−0.09780	0.02880	0.02188
$\Delta E = E_{\text{H}} - E_{\text{L}}$	−0.11285	−0.34856	−0.34603

Table 5b
Chemical potential, hardness and electrophilicity index by HF/6-31G(d,p), HF/6-311G(d,p) and B3LYP methods for (*E*)-1-4-NBTCH.

Parameters	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	HF/6-311G(d,p)
$\mu = -\chi$	−0.1542	−0.1455	−0.1511
η	0.0564	0.1743	0.1730
ω	0.2107	0.0607	0.0660

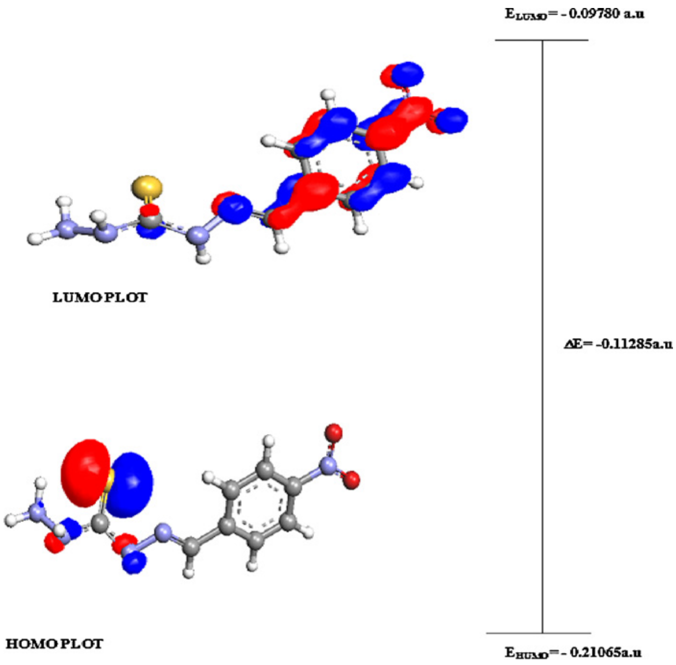

Fig. 4. The atomic orbital composition of the molecular orbital for (*E*)-1-4-NBTCH.

The global hardness is defined as

$$\eta = \frac{1}{2}\left(\frac{\delta^2 E}{\delta N^2}\right) V(r)\eta = \frac{1}{2}(I - A)h = \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}) \tag{6}$$

This measures the capacity of electrophile to accept the maximal number of electrons from the neighboring reservoir of electron i.e., a fractional or more than one electron. Using the above three Eqs. (4)–(6) the chemical potential, hardness and electrophilicity index have been calculated for (*E*)-1-4-NBTCH and their values are shown in Table 5b. The atomic orbital's compositions of the frontier molecular orbital are sketched in Fig. 4.

4.6. Thermodynamic parameters

Thermodynamic parameters are presented in Table 6. Scale factors have been recommended [50] for an accurate prediction

Table 6
Theoretically computed energies, zero-point vibrational energies (kcal/mol), rotational constants, entropies and dipole moment for (*E*)-1-4-NBTCH.

Parameters	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	HF/6-311G(d,p)
Total energies	−1132.28	−1127.18	−1127.36
Zero point energy	114.55	124.08	123.44
Rotational constants	1.76321	1.80483	1.81194
	0.14152	0.14450	0.14444
	0.13158	0.13412	0.13412
Entropy			
Total	127.871	125.109	125.397
Translational	42.316	42.316	42.316
Rotational	33.548	33.485	33.482
Vibrational	52.007	49.308	49.600
Dipole moment (*D*)	5.860	6.9424	7.0979

Table 7
Mulliken atomic charges for (*E*)-1-4-NBTCH.

Atoms	Charges	Atoms	Charges
C1	−0.091	N14	−0.207
C2	−0.120	N15	−0.364
C3	0.110	C16	0.357
C4	−0.144	H17	0.265
C5	−0.094	H18	0.262
C6	0.247	H19	0.274
H7	0.144	N20	−0.423
H8	0.145	N21	−0.418
H9	0.095	S22	−0.196
H10	0.138	N23	0.385
C11	0.102	O24	−0.401
H12	0.073	O25	−0.395
H13	0.256		

in determining the zero-point vibration energies (ZPVE) and the entropy, $S_{\text{vib}}(T)$. The variation in the ZPVE seems to be insignificant. The total energies and the change in the total entropy of (*E*)-1-4-NBTCH at room temperature at different methods are also presented.

In the present investigation, total energy as well as the zero-point vibrational energy of (*E*)-1-4-NBTCH increases at room temperature at different methods is also presented. Among the two methods, B3LYP/6-31G(d,p) shows minimum total energy for the title compound is −1132.283554 a.u.

4.7. Charge distribution

The charge distribution of the molecule has calculated on the basis of Mulliken method [51] using B3LYP/6-31G(d,p) level calculation. This calculation depicts the charges of the every atom in the molecule. Distribution of positive and negative charges is the vital to increasing or decreasing of bond length between the atoms. The survey of literature reveals that effective atomic calculations gave an important role in the application of chemical calculation to molecular system because of atomic charges, dipole moment, molecular polarizability, electronic structure, acidity–basicity behaviour and more lot of properties of molecular system [51].

Mulliken atomic charges and plot has shown in Table 7 and Fig. 5. The Mulliken scheme places the negative charge more or less evenly on C1, C2, C4, C5, N14, N15, N20, N21, S22, O24 and O25 atoms and splits the positive charge among the all hydrogen atom and some of the C3, C6, C11 and N23 atoms. Mulliken population analysis compute charges by dividing orbital overlap evenly between the two atoms involved.

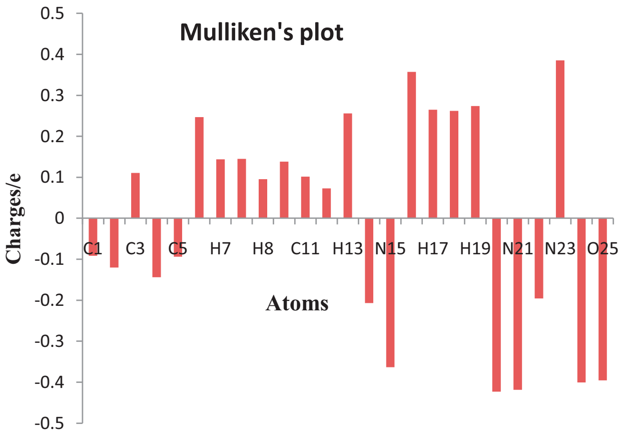

Fig. 5. The atomic charge plot of (*E*)-1-4-NBTCH.

5. Conclusion

The compound was derived from 4-nitrobenzaldehyde and thiocarbohydrazide by condensation reaction. Theoretical spectral frequencies are in good agreement with experimental data of FT-IR and FT-Raman. NBO reveals that charge transfer from LPN15, LPN20, LPS22 to its antibonding acceptor σ^*C16–S22, σ^*C16–S22, σ^*C16–N15 is about 43.30, 17.22 and 13.62 kcal/mol, respectively. The charge transfer from lone pair of atom to its antibonding orbital is more. The HOMO–LUMO energy gap strongly supports the presence of intramolecular energy transfer within the molecule. The calculated first order hyperpolarizability (2.8×10^{-30} esu) of (*E*)-1-NBTCH is six times greater than urea.

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