

Vibrational analysis of 1-Methyl-3-phenylthiourea- A density functional theory based study

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This work deals with the theoretical study on the molecular structure and vibrational spectra of 1-Methyl-3-phenylthiourea. The theoretical spectra were interpreted with the aid of normal mode analysis following full structure optimization based on the density functional theory and 6-311G (d, p) basis set combination.

The thermodynamic calculations related to the title compounds were also performed at B3LYP/6-311G (d, p) level of theory. The molecular HOMO, LUMO composition, energy gap, and MESP contours have also been drawn to explain the activity of 1-Methyl-3-phenylthiourea.

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Introduction

Urea or caramide is an organic compound with the chemical formula CO (NH₂)₂. The molecule has two —NH₂ groups joined by a carbonyl (C=O) functional group. Urea serves an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water and practically non-toxic [1]. Thiourea is the analogue compound to urea with Replacement of oxygen atom in urea by sulphur atom, also thiourea have a considerably wide range of applications. The properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen [2]. Thiourea compounds works as building blocks in the synthesis of heterocyclic compounds [3]. Thiourea and urea derivatives show a broad spectrum of biological activities as anti-HIV, antiviral, HDL-elevating, antibacterial and analgesic properties [4-7] Acyl thiourea derivatives are well known for wide range of biological activities like bactericidal, fungicidal, herbicidal, insecticidal action and regulating activity for plant growth [8, 9]. In addition, benzoyl thiourea derivatives were often used in analytical and biological applications [10].

As a part of our ongoing research [11-18], the main objective of the present study is to investigate in detail the vibrational spectra of important biological molecule 1-Methyl-3-phenylthiourea. To the best of our knowledge no detailed DFT calculations have been performed on 1-Methyl-3-phenylthiourea so far in the literature.

Computational Methods

Initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface. The gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [19] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [20] has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, and energies of the optimized structures, using GAUSSIAN 09 [21]. The calculated vibrational frequencies have

also been scaled by a factor of 0.963 [22]. By combining the results of the GAUSSVIEW'S program [23] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. We used this approach for the prediction of IR frequencies of title compound and found it to be very straightforward. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for anharmonicity. A number of studies [24, 25] have been carried out regarding calculations of vibrational spectra by using B3LYP methods with 6-311 G (d, p) basis set. The scaling factor (0.963) was applied successfully for B3LYP method and was found to be easily transferable in a number of molecules. Thus vibrational frequencies calculated by using the B3LYP functional with 6-311G (d, p) as basis set, can be utilized to eliminate the uncertainties in the fundamental assignment in the IR spectra.

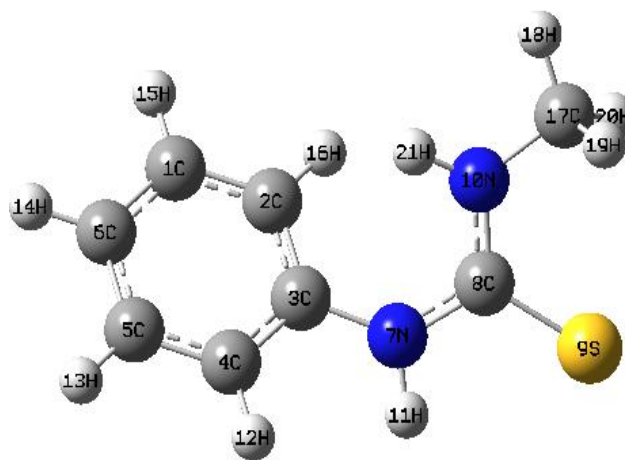


Fig. 1 Model molecular structure of 1-Methyl-3-phenylthiourea

Result and Discussions

Optimization

Optimized parameters calculated by B3LYP method with 6-31G (d, p) as basis set are listed in Table 1 and are in accordance with the atom numbering scheme as shown in Figure 1.

After geometry optimization local minimum energy obtained for structure optimization of 1-Methyl-3-phenylthiourea with 6-311G (d, p) basis set is approximately total energy = -818.59520141 a.u. The (C-C) bond length varies between 1.384Å- 1.0863Å, while (C-H) bond length, and is fixed at 1.086Å. (C-N) bond length presented at 1.326Å, while (C-S) bond length is at 1.4047Å. The (C-C-C) bond angle varies between 119.1- 122.2, while (C-C-H) bond angle is at 120.0- 130.2897. (C-C-N) bond angle presented at 119.64.

Atomic charge, Polarizability, Hyper polarizability and Thermodynamic Properties

The Mullikan atomic charges for all atoms of the 1-Methyl-3-phenylthiourea compound are calculated by B3LYP, methods with 6-31G (d, p) as basis set in gas phase and are presented in Table 2.

Dipole moment (μ), polarizability $\langle\alpha\rangle$ and total first static hyper polarizability β [26, 27] are also calculated (In Table 5 and 3) by using density functional theory. They can be expressed in terms of x, y, z components and are given by following equations 1, 2 and 3-

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \text{----- (1)}$$

$$\langle\alpha\rangle = 1/3 [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \text{----- (2)}$$

$$\beta_{\text{Total}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \\ = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzx} + \beta_{zxy})^2]^{1/2} \text{--- (3)}$$

The β components of Gaussian output are reported in atomic units.

Where (1 a.u. = 8.3693X10⁻³³ e.s.u.). For 1-Methyl-3-phenylthiourea, the calculated dipole moment value is 4.2863 Debye. Having higher dipole moment than water (2.16 Debye), 1-Methyl-3-phenylthiourea can be used as better solvent. As we see a greater contribution of α_{xx} in molecule which shows that molecule is elongated more towards X direction and more contracted to X direction. Perpendicular part Z contributes less part of polarizability of molecule. β_{xxx} , β_{xyy} contribute larger part of hyper polarizability in the molecule. This shows that XYZ plane and X-axis more optical active in these direction.

Several calculated thermodynamic properties based on the vibration analysis at B3LYP, 6-311G (d, p) level, like internal thermal energy (E), constant volume heat capacity CV, and entropy S, have been calculated and listed in table (4). At the room temperature, conduction band is almost empty so electronic contribution in total energy is negligible. Thermodynamic parameters clearly indicate that vibration motion plays a crucial role in assessing thermo dynamical behavior of title compounds. The calculated dipole moments at B3LYP/6-311G (d, p) level for 1-Methyl-3-phenylthiourea.

Table 1 Bond lengths (Å) and bond angles of 1-Methyl-3-phenylthiourea

S.NO	PARAMETER	EXPERIMENTAL VALUE	CALCULATED VALUE
BOND LENGTH			
	C ₁ -C ₂	1.384	1.3953
	C ₁ -C ₆	1.353	1.3948
	C ₁ -H ₁₅	0.9300	1.086
	C ₂ -C ₃	1.376	1.4047
	C ₂ -H ₁₆	0.9300	1.0845
	C ₃ -C ₄	1.366	1.4037
	C ₃ -N ₇	1.427	1.4139
	C ₄ -C ₅	1.393	1.3924
	C ₄ -H ₁₂	0.9300	1.0863
	C ₅ -C ₆	1.365	1.3967
	C ₅ -H ₁₃	0.9300	1.0859
	C ₆ -H ₁₄	0.9300	1.3953
	N ₇ -C ₈	1.342	1.3948
	N ₇ -H ₁₁	0.81	1.086
	C ₈ -S ₉	1.6964	1.4047
	C ₈ -N ₁₀	1.326	1.0845
	N ₁₀ -C ₁₇	1.455	1.4037
	N ₁₀ -H ₂₁	0.77	1.4139
	C ₁₇ -H ₁₈	0.9600	1.0925
	C ₁₇ -H ₁₉	0.9600	1.0955
	C ₁₇ -H ₂₀	0.9600	1.0918
BOND ANGLE			
	C ₂ -C ₁ -C ₆	120.2	119.194
	C ₂ -C ₁ -H ₁₅	119.9	120.0809
	C ₆ -C ₁ -H ₁₅	119.9	119.9567
	C ₁ -C ₂ -C ₃	120.0	120.1149
	C ₁ -C ₂ -H ₁₆	120.0	119.8914
	C ₃ -C ₂ -H ₁₆	120.0	119.1802
	C ₂ -C ₃ -C ₄	119.74	122.2767
	C ₂ -C ₃ -N ₇	120.57	118.4796
	C ₄ -C ₃ -N ₇	119.64	120.3323
	C ₃ -C ₄ -C ₅	119.6	119.2788
	C ₃ -C ₄ -H ₁₂	120.0	120.3873
	C ₅ -C ₄ -H ₁₂	120.0	120.453
	C ₄ -C ₅ -C ₆	120.2	119.4099
	C ₄ -C ₅ -H ₁₃	119.9	120.1328
	C ₆ -C ₅ -H ₁₃	119.9	119.3421
	C ₁ -C ₆ -C ₅	120.2	120.3373
	C ₁ -C ₆ -H ₁₄	119.9	120.3187
	C ₅ -C ₆ -H ₁₄	119.9	130.2897
	C ₃ -N ₇ -C ₈	127.17	117.3121
	C ₃ -N ₇ -H ₁₁	115.2	112.1821
	C ₈ -N ₇ -H ₁₁	117.4	119.7142
	N ₇ -C ₈ -S ₉	119.98	116.6169
	N ₇ -C ₈ -N ₁₀	118.32	123.6663
	S ₉ -C ₈ -N ₁₀	121.70	123.1794
	C ₈ -N ₁₀ -C ₁₇	123.87	117.7148
	C ₈ -N ₁₀ -H ₂₁	117.0	117.374
	C ₁₇ -N ₁₀ -H ₂₁	119.0	108.0581
	N ₁₀ -C ₁₇ -H ₁₈	109.5	111.7646
	N ₁₀ -C ₁₇ -H ₁₉	109.5	110.1011
	N ₁₀ -C ₁₇ -H ₂₀	109.5	109.5386
	H ₁₈ -C ₁₇ -H ₁₉	109.5	109.4975
	H ₁₈ -C ₁₇ -H ₂₀	109.5	107.865
	H ₁₉ -C ₁₇ -H ₂₀	109.5	119.194

Table 2 Mulliken atomic charges of 1-Methyl-3-phenylthiourea

S.NO.	ATOMS	ATOMIC CHARGES
1.	C	-0.093785
2.	C	-0.124620
3.	C	0.271740
4.	C	-0.105024
5.	C	-0.089532
6.	C	-0.083136
7.	N	-0.588305
8.	C	0.336260
9.	S	-0.315114
10.	N	-0.500655
11.	H	0.286870
12.	H	0.095868
13.	H	0.096334
14.	H	0.092125
15.	H	0.095537
16.	H	0.112862
17.	C	-0.159829
18.	H	0.104266
19.	H	0.141826
20.	H	0.157810
21.	H	0.268498

Table 3 Polarizability and Hyperpolarizability of 1-Methyl-3-phenylthiourea

Polarizability	
α_{xx}	-78.8399
α_{xy}	8.4686
α_{yy}	-65.1710
α_{yz}	-1.4393
α_{zz}	-74.0525
α_{zx}	1.6437
$\alpha = 72.6873$	
Hyper Polarizability	
β_{xxx}	-64.6317
β_{xxy}	28.1988
β_{xyy}	-4.8421
β_{yyy}	7.2550
β_{zzz}	2.7864
β_{xzz}	12.5489
β_{xzz}	2.4396
β_{yzz}	3.7260
β_{yyz}	2.9949
β_{xyx}	8.2112
β	79.7786

5

Table 4 Thermodynamic properties of 1-Methyl-3-phenylthiourea

PARAMETER	E (Thermal) Kcal/Mol	C_v Cal/Mol- Kelvin	S Cal/Mol- Kelvin
Total	113.854	39.587	103.346
Translational	0.889	2.981	41.230
Rotational	0.889	2.981	30.874
Vibrational	112.076	33.626	31.242

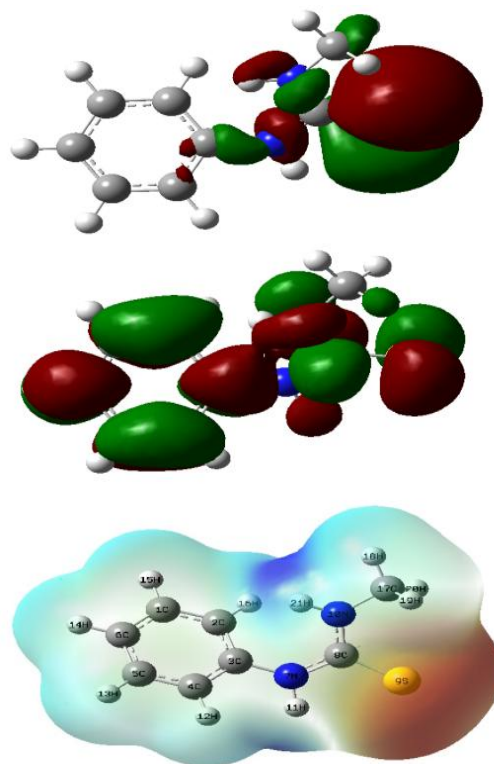
Electronic properties

The interaction with other species in a chemical system is also determined by frontier orbital's, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gap

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helps to distinguish the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gap is more polarized having more reactive part as far as reaction is concerned [28]. The frontier orbital gap in case of the given molecules is 4.735 eV, for 1-Methyl-3-phenylthiourea given in Table (5).

The contour plots of the HOMO, LUMO and MESP structures of the molecule are shown in Figure 2. The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative, and neutral electrostatic potential region in terms of grading and is very useful in the investigation of molecular structure with its physiochemical property relationship [29, 30].

**Fig. 2** HOMO (Left) - LUMO (Right) and MESP (Below) pictures of 1-Methyl-3-phenylthiourea**Table 5** Total energy, Dipole Moment, HOMO, LUMO and Energy gap of 1-Methyl-3-phenylthiourea

PARAMETERS	VALUE
Total Energy E (a.u.)	-818.59520141
Dipole moment (Debye)	5.3058
HOMO	-0.20186
LUMO	-0.02777
Frontier orbital Energy Gap (eV)	-0.17409 a.u (4.735248 eV)

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Table 6 Calculated Wavenumbers and its respective IR intensity of 1-Methyl-3-phenylthiourea

FREQUENCY	I.R. INTENSITY	VIBRATIONAL ASSIGNMENT
42	2.7161	MOLECULE TWIST FROM MIDDELE
53	1.6739	MOLECULE TWIST FROM MIDDELE
105	0.7092	MOLECULE BAND FROM MIDDLE
115	0.668	TWIST(NH ₃)
167	7.1887	TWIST(NH ₃)
221	0.8401	MOLECULE TWIST FROM MIDDELE
253	7.5491	MOLECULE BAND FROM MIDDELE
292	2.0515	MOLECULE BAND FROM MIDDELE + β (C-N-CH ₃)
344	9.7253	MOLECULE BAND FROM MIDDELE
400	9.8661	γ (C-C-H)
447	69.0333	ω (N ₁₀ -H ₂₁)
486	5.1583	γ (C-C-H)
506	106.1294	ω (N ₇ -H ₁₁)
559	0.8768	τ (IN WHOLE MOLECULE)
596	8.7638	τ (IN WHOLE RING)
604	12.3757	τ (IN WHOLE RING)
610	6.2495	τ (IN WHOLE RING)
682	13.2451	γ (C-C-H)
726	36.8895	γ (C-C-H)
773	10.318	β (N7-C8-N10)+ γ (C-C-H)
813	0.0326	β (C-C-C) IN RING
824	1.9039	β (C-C-C) IN RING
883	3.279	β (C-C-H)
933	0.1955	γ (C-C-H)
956	0.322	γ (C-C-H)
974	0.2512	RING DEFORMATION
1013	0.1501	β (C-C-H)
1037	65.0175	β (C ₈ -N ₁₀ -H ₂₁) + TWIST(NH ₃)
1068	12.0575	β (C-C-H)
1107	7.1532	Twist(NH ₃)
1132	12.6551	Twist(NH ₃)
1141	0.5228	β (C-C-H) in ring
1158	2.8769	β (C-C-H) in ring
1195	80.9859	β (C-C-C) in ring + β (C ₈ -N ₁₀ -C ₁₇)+ β NH ₃
1214	108.4232	β (C ₃ -N ₇ -H ₁₁)+ β (C-C-H)
1287	138.899	β (C-C-H) in ring
1305	13.42	RING DEFORMATION
1328	95.7902	β (C-C-H) in ring + ν (C-N)
1404	26.287	S(NH ₃)+ β (C-C-H) in ring
1425	11.2914	Twist(NH ₃)
1439	33.1324	β (C-C-H) in ring+ β (C ₈ -N ₁₀ -H ₂₁)
1458	1.2142	S(H ₁₉ -C ₁₇ -H ₂₀)
1474	0.1652	β (C-C-H) in ring
1487	456.2491	β (C ₈ -N ₁₀ -H ₂₁)+ ω (N ₇ -H ₁₁)+ β (C-C-H) in ring
1513	292.9232	β (C-N-H)
1574	13.9085	ν (C-C) in ring+ ω (N ₇ -H ₁₁)
1592	46.272	ν (C ₁ -C ₂)+(C ₄ -C ₅)
2927	43.6446	ν (H ₁₈ -C ₁₇)+(C ₁₇ -H ₂₀)+(C ₁₇ -H ₁₉)
2996	19.35	ν (H ₁₈ -C ₁₇)+(C ₁₇ -H ₂₀)+(C ₁₇ -H ₁₉)
3025	10.7749	ν (H ₁₈ -C ₁₇)+(C ₁₇ -H ₂₀)
3056	5.0159	ν (C-H) in ring
3062	1.6278	ν (C-H) in ring
3071	17.5671	ν (C-H) in ring
3082	18.8836	ν (C-H) in ring
3088	4.5052	ν (C-H) in ring
3460	41.828	ν (N ₁₀ -H ₂₁)
3483	46.0989	ν (N ₇ -H ₁₁)

Assignment of fundamentals

1-Methyl-3-phenylthiourea has 21 atoms with 57 normal modes of vibration. We made a reliable one-to-one correspondence between the fundamentals and the frequencies calculated by DFT (B3LYP) methods. The relative band intensities are also very satisfactory along with their position. Some important modes are discussed hereafter. The harmonic vibrational frequencies, calculated for the title molecule with vibrational assignments are given in Table (6).

Vibrational modes description

Spectral region above 2800 cm⁻¹: The C-H stretching vibrations are generally observed in the region 2800-3100cm⁻¹. Accordingly, in the present study for 1-Methyl-3-phenylthiourea, the C-H stretching vibrations are calculated at 2927-3088 cm⁻¹, respectively.

Spectral region from 1000 cm⁻¹ to 2300 cm⁻¹: In the present study, Ring Deformation in molecule are observed at 1305, 974 cm⁻¹. Some in plane and out of plane bending vibrations are also presented in this region also.

Spectral region below 1000 cm⁻¹: C-H wagging is calculated in the region 447, and 506 cm⁻¹. Out of plane bending in C-C-H is calculated at 400, 486, 682, 726, 933, 956 cm⁻¹.

Conclusion

Attempts have been made in the present work for the proper frequency assignments for 1-Methyl-3-phenylthiourea. The equilibrium geometries and harmonic frequencies of 1-Methyl-3-phenylthiourea were determined and analysed at DFT level of theory utilizing 6-311 G (d, p) as the basis set. The vibrational frequency calculation proved that both structures are stable (no imaginary frequency). Electronic properties show the reactivity of molecule with the help of HOMO-LUMO gap. Hyperpolarizability is mainly controlled by the planarity of the molecules, the donor and acceptor strength, and bond length alteration. The values of hyperpolarizability indicate a possible use of these compounds in electrooptical applications. The present work might encourage the need for an extensive study by the experimentalists interested in the vibrational spectra and the structure of this compound.

Notes and References

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