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Vibrational, Non-Linear Optical, Thermal And Energy Gap Studies On 4-(3-Bromophenyl)-2-Phenyl-1,3-Thiazole (BPPT): A Density Functional Theory Approach

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***Abstract*- Theoretical studies have been carried out on BPPT using DFT-B3LYP method using 6-311+G basis set. The geometrical parameters of the title molecule, like bond length, bond angle and dihedral angles have been calculated and studied. The IR wavenumbers have been calculated theoretically using above mentioned method and are compared with the experimental IR wavenumbers. From this analysis, it can be seen that the vibrational frequencies obtained from B3LYP method are in good agreement with the experiment. Nonlinear optical properties like dipole moment, hyper polarizabilities and thermal properties like rotational constants, zero point vibrational energies are calculated using the same methodology. The effect of temperature on various thermodynamic properties have been calculated theoretically and reported. The frontier molecular orbital studies have been carried out to explain the charge transfer in title molecule.**

Index Items - Entropy, FT-IR spectra, Hyperpolarizability, Homo-Lumo energy gap.

I. INTRODUCTION

Thiazoles that contain sulfur atom are important class of heterocyclic compounds. These are present in many natural/synthetic products, which have a wide range of pharmacological activities [1] and also find various applications in the other fields such as polymers [2], liquid crystals [3]. Due to its fascinating biological activity, it is very interesting to study the geometrical, vibrational, thermal and nonlinear optical properties of the title molecule. Density functional theory (DFT) is becoming more useful to experimentalists in computing the geometrical parameters and other properties like vibrational, thermal, nonlinear, optical etc. of polyatomic molecules [4].

The title molecule (fig. 1.) considered for this study has been synthesized previously and reported by Pavan Kumar etal [5]. The geometrical parameters (like bond lengths, bond angles and dihedral angles), non-linear optical properties (like dipole moment, first hyperpolarizability and total hyperpolarizability), thermodynamic parameters (like total energy (Etot), zero-point vibrational energy (ZPVE), heat capacities (CV), entropy (S), total thermal energy (□tot), rotational constants (rC) and rotational temperatures (rT) and HUMO-LUMO gap energy (ΔEg) have been calculated theoretically and reported. The effect of temperature on some thermodynamic properties at various temperatures have been calculated theoretically and reported.

II. COMPUTATIONAL DETAILS

The Optimized structure parameters and vibrational frequencies of BPPT have been studied by B3LYP method using 6-311+G basis set. The quantum chemical calculations have been performed with Gaussian 03W software [6]. During optimization the atomic positions of the molecule in all possible geometrical conformations have been fully relaxed, and only the lowest-lying minima is reported. Frequency calculations have been carried out to ensure that the optimized geometry has all positive frequencies and thus is a minimum on the potential energy surface.In scaled quantum mechanical method, the systematic errors of the computed harmonic force field are corrected by a few scale factor (0.97) which are found to be well transferable between chemically related molecules and were recommended for general use [7] The assignments of the calculated wave numbers are made with a high degree of

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confidence by the VEDA 4 program [8] and animation option of Gauss View 3.0 package which gives a visual presentation of the vibrational modes and frontier molecular orbitals like HOMO and LUMO [9].

III. GEOMETRIC STRUCTURAL ANALYSIS:

Since the molecular parameters are controlled by the molecular geometry, the crucial step for the calculation of IR spectra is the geometry optimization of the molecule. The optimized bond length, bond angle and dihedral angles of BPPT are listed in Table 1. All the bond lengths in thiazole ring are in the range of 1.85 – 1.30Å which are in good agreement with the reported data for thiazole [5] and substituted thiazole [5] and bond lengths in C6H5 part of the title molecule are in the range 1.39-1.41 Å which are in good agreement with reported values of benzene and substituted benzenes in literature [10].

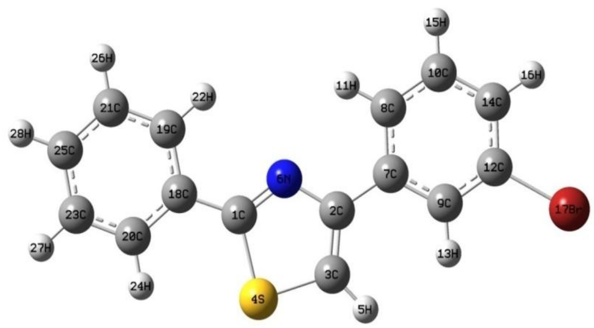

Fig 1: Optimized structure of BPPT

Table. 1: The geometrical parameters of the BPPT at B3LYP/6-311+G level

Bond length(Å)		Bond angle (°)				Dihedral angle (°)	
R(1-4)	1.85	A(4-1-6)	122	A(14-12-17)	120.4	D(1,6,2,7)	179.9
R(1-6)	1.3	A(4-1-18)	87	A(12-14-16)	118.7	D(6,2,7,8)	0.025
R(1-18)	1.46	A(1-4-3)	125.8	A(19-18-20)	120.5	D(2,7,8,10)	179.9
R(2-3)	1.37	A(6-1-18)	114.6	A(18-19-21)	120.1	D(10,14,12,17)	179.9
R(2-6)	1.4	A(1-6-2)	119.1	A(18-19-22)	120.9	D(2,7,9,12)	-179.9
R(2-7)	1.48	A(1-18-19)	122	A(18-20-23)	120.3	D(4,3,2,7)	-179.9
R(3-4)	1.79	A(1-18-20)	114.4	A(18-20-24)	119.6	D(3,4,1,18)	-180.0
R(3-5)	1.07	A(3-2-6)	127	A(21-19-22)	119.3	D(1,18,20,23)	180.0
R(7-8)	1.41	A(3-2-7)	111.7	A(19-21-25)	120.2	D(1,18,19,21)	180.0
R(7-9)	1.41	A(2-3-4)	129.4	A(19-21-26)	119.6	D(2,6,1,18)	-179.9
R(8-10)	1.39	A(2-3-5)	118.6	A(23-20-24)	120	D(6,2,7,9)	-178.3
R(8-11)	1.08	A(6-2-7)	120.1	A(20-23-25)	119.7		
R(9-12)	1.39	A(2-7-8)	121.2	A(20-23-27)	120.2		
R(9-13)	1.08	A(2-7-9)	118.9	A(25-21-26)	120.2		
R(10-14)	1.4	A(4-3-5)	118.7	A(21-25-23)	120.1		
R(10-15)	1.08	A(8-7-9)	120.5				
R(12-14)	1.39	A(7-8-10)	118.8				
R(12-17)	1.08	A(7-8-11)	119.8				
R(14-16)	1.41	A(7-9-12)	120.8				
R(18-19)	1.41	A(7-9-13)	120.8				
R(18-20)	1.39	A(10-8-11)	120.8				
R(19-21)	1.39	A(8-10-14)	119.8				
R(19-22)	1.08	A(8-10-15)	119.3				
R(20-23)	1.4	A(12-9-13)	121.8				
R(20-24)	1.08	A(9-12-14)	119.4				
R(21-25)	1.4	A(9-12-17)	118.4				
R(21-26)	1.08	A(14-10-15)	121				
R(23-25)	1.4	A(10-14-12)	120.6				
R(23-27)	1.08	A(10-14-16)	118.9				

IV. VIBRATIONAL ANALYSIS:

CH stretching:

The CH stretching vibrations are characteristic vibrations of molecules in which aromatic compounds are present. In case of title molecule, these vibrations have been observed at 3108 and 3050 cm^{-1}[11] and the calculated values falls in the range 3176-3068 cm^{-1}, which are in good agreement with observed and reported values[5]. The individual peak for CH stretch on thiazole part has not been observed separately but the calculated vibrational mode is present at 3176Cm^{-1} which in good agreement with the reported values.

Table 2: Calculated and observed vibrational frequencies (cm-1) and assignments with potential energy distribution (PED) of BPPT.

Mode No.	Calculated unscaled	scaled	Experimental IR	Assignment(%PED)
1	3274	3176		v-C_3H_5
2	3219	3122		v-ph-CH
3	3208	3112		v-ph-CH
4	3208	3112		v-ph-CH
5	3204	3108	3108	v-ph-CH
6	3195	3099		v-ph-CH
7	3182	3087		v-ph-CH
8	3175	3080		v-ph-CH
9	3171	3076		v-ph-CH
10	3163	3068	3050	v-ph-CH
11	1640	1590	1594	v-ph-C=C
12	1634	1585		v-ph-C=C
13	1614	1566		v-ph-C=C
14	1599	1551		v-ph-C=C
15	1560	1513		v-C_1-N_6(78)+v-C_{18}-C_1(55)
16	1551	1504	1504	v-C_2=C_3(72)+v-C_2-C_7(25
17	1525	1479	1469	β-CH(45)+v-C_1=N_6(30)
18	1497	1452		v-C_3=C_2(45)+β-CH(50)
19	1489	1445	1436	βCH(78)+v-ph-C=C(10)
20	1460	1416	1395	β-CH(55)+v-ph-C=C(45)
21	1382	1341		β-CH(65)
22	1356	1316	1311	β-CH(65)
23	1338	1298		v-ph-C=C(63)+βCH(40)
24	1325	1285	1282	v-phC=C(63)+βCH(40)
25	1307	1268		v-N_6-C_2(80)+β-CH(15)
26	1255	1217	1233	v-C_{18}-C_1(35)+βCH(25)
27	1229	1192	1198	β-CH(40)+βC_3H_5(59)
28	1228	1191		β-CH(52)+βC_3H_5(50)
29	1217	1180		βCH(65)
30	1212	1176		βCH(72)
31	1125	1091	1101	βCH(81)
32	1117	1083		βCH(51)
33	1097	1064	1049	βCH(35)+βC_3H_5(25)
34	1066	1034		βC_3H_5(80)+δ-ring(19)
35	1054	1022		δ-ring(36)
36	1032	1001	1001	γCH(58)
37	1028	997		δ-ring- dia(68)
38	1028	997		γCH(58)
39	1021	991		δ-ring- dia(68)
40	1016	986	973	γCH(65)
41	969	940		γCH(65)
42	967	938		γCH(67)
43	966	937		ring breathing(33)+v-C_1=S_4(23)
44	926	898	896	γCH(90)

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45	905	878		δ -thiazolering(48)
46	877	851	827	γCH(65)
47	830	805		γCH(65)
48	807	782		γCH(65)
49	805	781	764	ν-S_4-C_3(65)+δ-ring-dia(22)
50	770	747	719	γC_3-H_5(65)+γCH(15)
51	718	696		γCH(45)
52	713	692		ν-C_{12}-Br_{17}(32)+ δ molecule(45)
53	712	691	686	γC_3-H_5(70)+γCH(23)
54	687	667		δ-ring-dia(45)
55	685	664		β-ring
56	680	659		δ-ring-dia(60)
57	649	629		δ-ring-dia(60)
58	618	600	593	δ-molecule (35)
59	601	583		β-molecule(62)
60	543	527	491	β-molecule(45)
61	496	481		rock-Ph-ring
62	466	452		β-molecule(25)
63	451	437		β-ring(25)
64	423	410	418	β-ring(25)
65	374	362		δ-molecule(33)
66	333	323		δ-molecule(33)
67	304	295		δ-molecule(33)
68	284	275		torsion-ring(22)
69	259	252		δ-molecule(22)
70	255	248		δ-molecule(22)
71	201	195		δ-molecule(22)
72	174	169		δ-ring(30)
73	115	112		δ-molecule(18)
74	113	109		δ-molecule(22)
75	77	75		δ-molecule(11)
76	57	55		δ-molecule(20)
77	29	28		δ-molecule(25)

ν: stretching; $ν_{as}$: asymmetric stretching; $ν_s$: symmetric stretching; γ: out-of-plane bending; β: in-plane bending; τ: tortion; δ: deformation; ω: wagging; ζ: twist; r: rock; s: scissor; *: thiazole group.

C=C stretching and CH bending vibrations:

In case of BPPT the ν-C=C vibrations have been observed at 1594,1504 and 1282Cm^{-1} vibrational modes(ref). According to literature these vibrations occurs in the region 1500 to 1680Cm^{-1} [12]. The calculated values for these vibrations are in the range of 1590-1504 cm^{-1}. The β-CH vibrational modes have been observed at 1436, 1395, 1311, 1198, 1049 and 1049 cm^{-1}[5] on thiazole part of the molecule and the calculated values occur in the region 1479-1034Cm^{-1} which is in good agreement with the observed and reported values (ref). The calculated values of γ- CH vibrational modes occurs in the range 1001-691cm-1 which are in good agreement with the observed vibrational modes which occurs at 1001, 973, 896, 827, 719 and 686 cm^{-1}[5] and reported values.

Other vibrations:

The Other vibrations namely ring deformation, ring bending, molecule deformations have been observed at 593, 491and 418cm-1. The calculated values for these vibrations are in good agreement with the reported and observed values [13]. The ν-S4-C3 vibrations have been observed at 719Cm-1 and the calculated value for this occurs at 781cm-1, which is in good agreement with the observed and reported value [5].

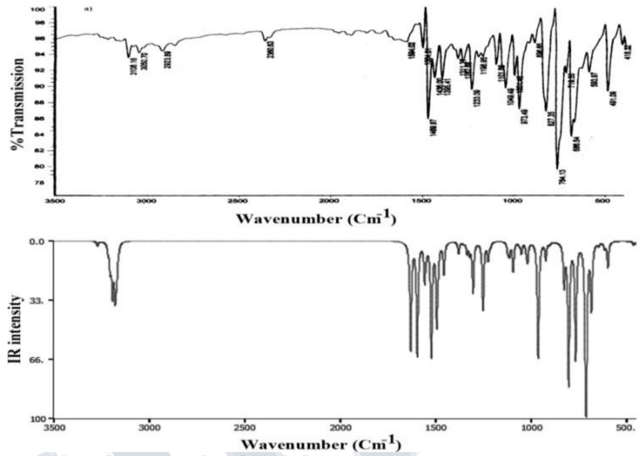

***Fig. 2:** - IR spectra of BPPT: (a) experimental FT-IR spectra[10] in KBr and (b) calculated spectra obtained from B3LYP/6- 311+G level theory.*

V. THERMAL PROPERTIES

The study of thermodynamic properties of organic molecules has its own importance in the research area. The Thermodynamic properties like total energy (Etot), heat capacities (CV) entropy (S) and total thermal energy (Єtot), rotational constants (rC) and rotational temperatures (rT) of BPPT have been calculated at constant pressure using the B3LYP/6-311+G optimized geometries and the results are tabulated in Table 3. Various thermodynamic properties have been calculated at different temperatures using the B3LYP/6-311+G optimized geometry and the results are tabulated in Table 4. It can be seen from the Table 4, that the thermodynamic function value increases with increasing the temperature and this may be attributed to the fact that the intensities of molecular vibration increases as the temperature increases [14]. The correlations between these thermodynamic properties and temperature are shown in Fig. 3. The empirical correlations between the thermodynamic properties and temperature are deduced as follows:

H=8 x 〖10〗^(-5) T^2+0.013T+256.9
C_V=-9 × 〖10〗^(-5) T^2+0.219T+0.485
E tot=8× 〖10〗^(-5) T^2-0.11T+128.1
S=0.189T+71.65

All the above-mentioned thermodynamic data may be useful in the field of thermodynamics, for further study on the title molecule.

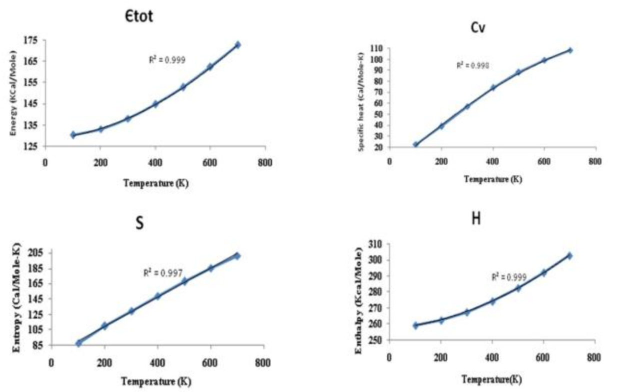

Fig. 3: Correlation graph between Temperature and Thermodynamic properties of BPPT

Table 3: Thermodynamic properties of BPPT at different temperatures at B3LYP/6-311+G level

T	ϵ_{tot}	C_v	S	H
100	130.3	22.8	87.9	259.3
200	133.3	39.0	109.9	262.5
300	138.2	57.2	130.0	267.6
400	144.8	74.2	149.4	274.4
500	152.9	88.4	168.0	282.7
600	162.4	99.6	185.5	292.4
700	172.8	108.6	201.8	303.0

T in Kelvin; ϵ_{tot} in Kcal/mol; Cv in cal/mol-K; S in Cal/mol-K; H in K cal/mol

VI. NLO PROPERTIES

In case of BPPT the non-linear optical properties like total dipole moment (μ_{tot}), mean polarizability (α_m), molecular first hyperpolarizability (β_μ), and total hyperpolarizability (β_{tot}) have been calculated using B3LYP/6-311+G optimized geometries. The values of all these properties have been calculated using standard equations available in literature [15]. The calculated dipole moment, mean linear polarizability, first hyperpolarizability and total polarizability values of **BPPT** listed in Table 5(1.07 Debye, 34.36 x 10^{-24} esu, 1.32 x 10^{-30} esu, 2.4 x 10^{-30} esu.

Table 4: The dipole moment (in Debye), polarizability (in esu), hyperpolarizabilities (in esu) tensors computed with the B3LYP/6-311+G method.

μ_x	-0.058	β_{xxx}	95.07
μ_y	-0.34	β_{xxy}	75.93
μ_z	-1.02	β_{xyy}	38.53
$\boldsymbol{\mu_{tot}}$	**1.07**	β_{yyy}	-3.41
		β_{xxz}	126.02
α_{xx}	207.69	β_{xyz}	-25.43
α_{xy}	42.32	β_{yyz}	-55.67
α_{yy}	144.79	β_{xzz}	-310.68
α_{xz}	-22.39	β_{yzz}	-73.73
α_{yz}	61.1	β_{zzz}	207.67
α_{zz}	343.1	$\boldsymbol{\beta_\mu}$	**$1.322x10^{-30}$**
$\boldsymbol{\alpha_m}$	**$34.36x10^{-24}$**	$\boldsymbol{\beta_{tot}}$	**$2.4x10^{-30}$**

VII. HOMO-LUMO ENERGY GAP (ΔE)

The frontier molecular orbitals namely highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) and their properties such as energy are very useful for physicists and chemists for evaluating the charge transfer within the molecule. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [16]. The energy gap between HOMO and LUMO explains the biological activity of the molecule, which is due to the change in partial charge and to the change in total dipole moment. The plots of HOMO, LUMOs and **ΔE** are shown in Fig. 5.

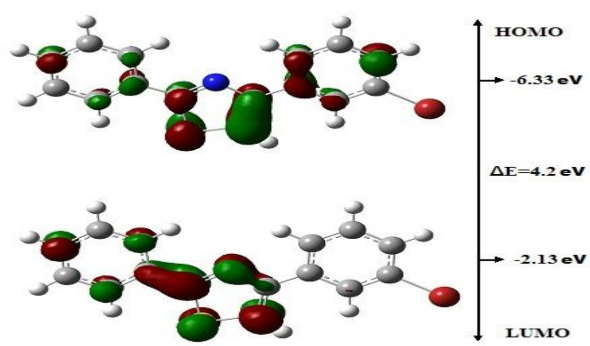

Fig 4 - Frontier molecular orbitals (HOMO and LUMO) and the energy gap (ΔE) of BPPT

The HOMO and LUMO energy calculated by B3LYP/6-311+G method in gas phase is given below.
HOMO energy (B3LYP) = -6.33eV
LUMO energy (B3LYP) = -2.13eV
HOMO–LUMO energy gap (B3LYP) = 4.2 eV

VIII.CONCLUSIONS

In the present study, the structural geometrical parameters, vibrational frequencies, thermodynamic and nonlinear optical properties of BPPT have been studied using B3LYP method with 6-311+G basis set. The structural parameters like bond length and angles obtained are in good agreement with reported values of thiazoles. It can be seen that the calculated vibrational frequencies of BPPT computed using DFT/B3LYP/6-311+G method are in good agreement with the experiment. The spectral frequencies have been calculated using above-mentioned method are compared with the observed spectra. The complete vibrational assignments of wavenumbers have been made on the basis of potential energy distribution and found to be in good agreement with the experiment. The thermodynamic properties have been calculated for the title molecule may be helpful in the estimation of chemical reaction directions. Using the B3LYP/6-311+G optimized geometry, the thermodynamic properties are calculated at constant pressure by varying the temperature and the correlation between them is found to be linear. The polarizability, first hyperpolarizability and total hyperpolarizability imply that the title molecule may be useful as a NLO material. Furthermore, from the molecular orbital analysis, it can be seen that there is a possibility of intermolecular charge transfer within the molecule. From these studies, it can be concluded that the theoretical methods are useful in predicting the geometrical, vibrational, optical, thermodynamic and charge transfer properties for the new molecule in advance.

IX. ACKNOWLEDGMENTS

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