

Ab initio and density functional studies on the structure and vibrational Spectra of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol

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Abstract— The molecular structure (bond distances and angles), dipole moment and vibrational spectroscopic data (vibrational frequencies, IR and Raman intensities) of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol were calculated using Hartree–Fock (HF) and density functional (DFT) with basis sets 6-31G* and 6-31+G*. This molecule was chosen as the model for the present study, because the synthesis and X-ray crystal structure analysis of a possible bioactive molecule, 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3 thiol have been reported. The theoretical results are discussed mainly in terms of comparisons with available experimental data. For geometric data, good agreement between theory and experiment is obtained for the HF and B3LYP levels with basis sets including diffuse functions. The calculated vibrational spectra were interpreted and band assignments were reported. In addition, ¹H- and ¹³C-nuclear magnetic shielding constants of this compound were calculated by employing the direct implementation of the gauge including-atomic-orbital (GIAO) method at the Hartree–Fock (HF) using 6-31G* basis set.

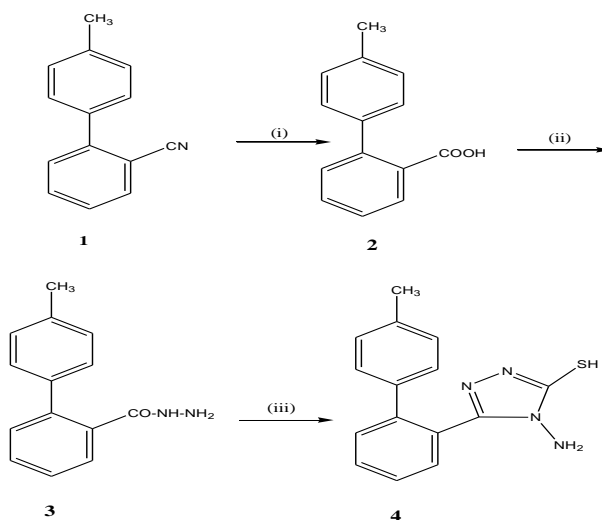
Keywords- DFT; FT-IR spectrum; HF; Vibrational assignments; 1, 2, 4-Triazole

1. Introduction

Compounds of 1, 2, 4-triazole derivatives exhibit diverse pharmacological activities [1] such as fungicidal, insecticidal, bactericidal, herbicidal, anti-tumour [2], anti-inflammatory [3], CNS stimulant [4]. They also find applications as dyes, lubricants, analytical reagents [5] and antiviral agents [6]. The complexes containing 1, 2, 4-triazole ligands possess specific magnetic properties [7]. The compound losartan potassium, a non-peptide small molecule bearing biphenyl aromatic group and imidazole, combines an angiotensin II receptor (type AT1) antagonist and diuretic property. In the light of the above observations, the incorporation of the active 1, 2, 4-triazole nucleus to the biphenyl ring is part of our continued effort towards the synthesis and study of the biological properties of condensed nitrogen and sulphur heterocycles [8–10]. In the present study we started the theoretical studies of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3 thiol. This molecule was chosen as the model for the present study, because the synthesis and X-ray crystal structure analysis of a possible bioactive molecule, 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3 thiol have been reported [11]. The theoretical results are discussed mainly in terms of comparisons with available experimental data.

2. Experimental

The synthesis of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol **4** was obtained by using 4-methyl-2-cyanobiphenyl as shown in Scheme 1. The synthesis of the title compound **4** involves the oxidation of nitrile to the corresponding acid **2**. The 4-methyl-2-biphenyl carboxylic acid is esterified and hydrazinated to obtain the pure crystalline hydrazide **3**. The crystalline hydrazide was reacted with carbon disulphide in the presence of alcoholic KOH to obtain potassium salt of thiocarbohydrazide followed by the addition of the hydrazine hydrate to obtain the title compound **4**. The melting points were determined on SELACO-650 hot stage apparatus and are uncorrected. IR (KBr) spectra were recorded on a Jasco FT/IR-4100 Fourier transform infrared spectrometer, ¹H NMR were recorded on Shimadzu AMX400, spectrometer by using CDCl₃ as solvent and TMS as an internal standard (Chemical shift in ppm). Elemental analyses were obtained on a vario-EL instrument. Thin layer chromatography (TLC) was conducted on 0.25mm silica gel plates (60F254, Merck). Visualization was made with ultraviolet light. All extracted solvents were dried over Na₂SO₄ and evaporated with a BUCHI rotary evaporator. Reagents were obtained commercially and used as received [11].



Scheme 1

(i) 30% NaOH, Methanol

(ii) H₂SO₄, Methanol; Ethanol, NH₂-NH₂

(iii) CS₂, KOH; NH₂-NH₂, Ethanol

3. Calculations Details

All the calculations were performed with the Gaussian 03W program package on a double Xeon/3.2 GHz processor with 8 GB Ram [12]. The molecular structure of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol, in the ground state are optimized by using the Hartree-Fock (HF)[13], density functional using Becke's three-parameter hybrid method[14] with the Lee, Yang, and Parr correlation functional methods[15](B3LYP) with the standard 6-31G* [16] and 6-31+G* basis sets. The vibrational frequencies were also calculated with these methods. The frequency values computed at these levels contain known systematic errors [17]. Therefore, we have used the scaling factor values of 0.9135, 0.9163, and 0.9806 and for HF and B3LYP, respectively. We have also calculated optimal scaling factors for all investigated methods. The assignment of the calculated wave numbers is aided by the animation option of GaussView 3.0 graphical interface for gaussian programs, which gives a visual presentation of the shape of the vibrational modes [18].

4. Results and Discussion

4.1 Geometric parameters

X-ray diffraction and calculated for the isolated state structures of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol molecules with atom numbering are presented in Fig. 1. The structure parameters is orthorhombic, the space group *Pbca*, with the cell dimensions $a = 11.2730(3)$ (Å), $b = 17.2450(15)$ (Å), $c = 7.4130(10)$ (Å), $\beta = 97.742(5)$ (°) and Volume (Å³). In this work, we performed full geometry optimization of the title compound. The main selected bond lengths and angles as well as torsion angles are collected in Table 1.

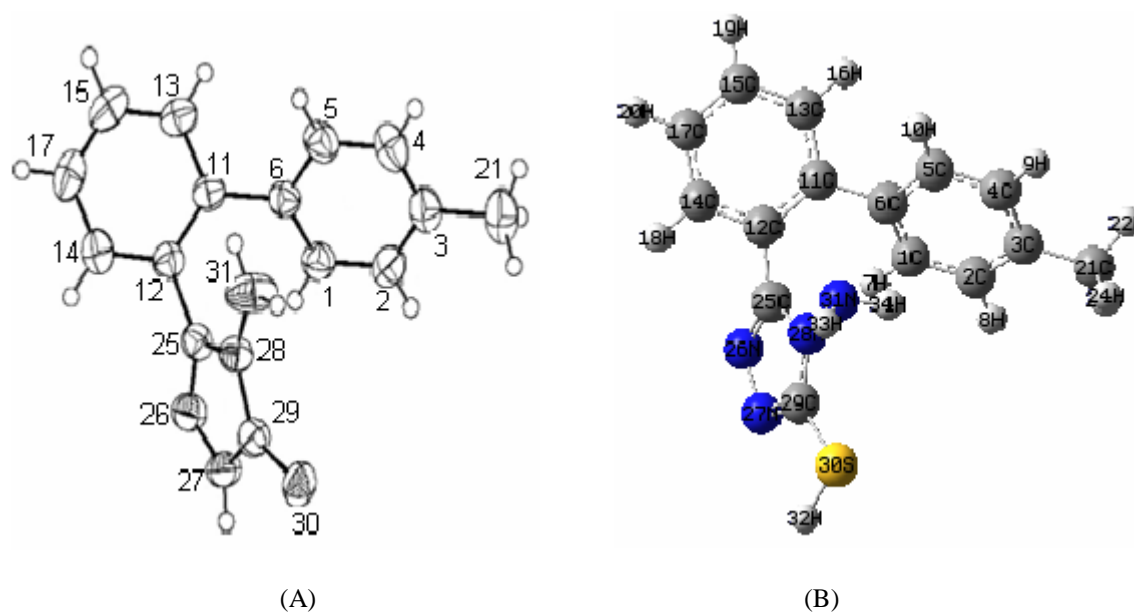


Figure 1. The structure of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol molecules: (A) X-ray experimental [11] with atom numbering; (B) calculated for the isolated molecules in the gas phase.

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Table 1. Optimized and experimental Bond Lengths (Å) and Angles (deg) of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol

Parameter	HF		B3LYP		Experimental	
	6-31G(d)	6-31+G(d)	6-31G(d)	6-31+G(d)		
Bond lengths (Å)						
1	C1-C2	1.387	1.386	1.395	1.395	1.387
2	C2-C3	1.387	1.392	1.400	1.403	1.392
3	C3-C4	1.392	1.390	1.403	1.402	1.382
4	C4-C5	1.382	1.387	1.393	1.396	1.386
5	C1-C6	1.389	1.393	1.404	1.406	1.394
6	C5-C6	1.393	1.391	1.405	1.405	1.392
7	C6-C11	1.494	1.495	1.489	1.490	1.489
8	C11-C12	1.399	1.400	1.415	1.415	1.405
9	C11-C13	1.391	1.393	1.404	1.405	1.386
10	C12-C14	1.389	1.390	1.402	1.403	1.400
11	C13-C15	1.384	1.385	1.393	1.395	1.386
12	C14-C17	1.383	1.384	1.392	1.394	1.380
13	C3-C21	1.511	1.511	1.511	1.511	1.508
14	C15-C17	1.383	1.385	1.395	1.396	1.376
15	C25-N26	1.283	1.283	1.315	1.315	1.305
16	N26-N27	1.369	1.369	1.389	1.388	1.373
17	C25-N28	1.366	1.367	1.382	1.384	1.367
18	N27-C29	1.278	1.279	1.309	1.310	1.334
19	N28-C29	1.357	1.357	1.373	1.374	1.374
20	C29-S30	1.759	1.758	1.767	1.765	1.679
21	N28-N31	1.379	1.380	1.398	1.398	1.399
22	C12-C25	1.481	1.481	1.474	1.474	1.475
Bond angles (°)						
1	C1-C2-C3	121.26	121.28	121.39	121.38	121.1
2	C2-C3-C4	117.84	117.77	117.68	117.62	117.6
3	C3-C4-C5	121.11	121.12	121.20	121.24	121.8
4	C2-C1-C6	120.82	120.85	120.88	120.93	121.1
5	C1-C6-C11	121.34	121.34	121.51	121.44	122.6
6	C6-C11-C12	122.79	122.79	123.06	122.98	121.8
7	C6-C11-C13	118.98	118.97	118.84	118.90	119.8
8	C12-C11-C13	118.20	118.21	118.04	118.06	118.4
9	C11-C12-C14	120.11	120.12	119.86	119.91	119.8
10	C11-C13-C15	121.41	121.42	121.66	121.64	121.2
11	C12-C14-C17	120.85	120.88	121.02	121.01	120.4
12	C2-C3-C21	121.42	120.90	121.38	121.01	120.8
13	C4-C3-C21	120.73	121.31	120.94	121.35	121.6
14	C11-C12-C25	122.54	122.50	123.22	122.92	121.3
15	C14-C12-C25	117.34	117.37	116.91	117.16	118.8
16	C4-C5-C6	120.96	121.01	121.08	121.08	120.7
17	C1-C6-C5	118.01	117.96	117.76	117.74	117.8
18	C5-C6-C11	120.62	120.68	120.69	120.79	119.6
19	C13-C15-C17	119.99	119.97	119.88	119.87	120.0
20	C25-N26-N27	108.32	108.35	108.38	108.38	104.0
21	C12-C25-N28	124.91	124.92	125.37	125.22	124.8
22	N26-C25-N28	109.43	109.40	109.24	109.19	110.1
23	N26-N27-C29	107.19	107.24	106.77	106.96	114.2
24	N27-C29-S30	127.36	127.22	127.88	127.61	130.5
25	C25-N28-N31	126.28	126.32	126.22	126.03	124.7
26	C25-N28-C29	104.33	104.38	104.69	104.79	109.4
27	N28-C29-S30	121.93	122.16	121.20	121.71	127.3

As follows from this comparison, the bond lengths and angles calculated for title compound show quite good agreement with experimental values. The agreement for bond angles is not as good as that for the bond distances (fig. 2). However, owing to our calculations, DFT method correlates well for the bond length and angle in

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comparison to the HF method. The largest difference between experimental and calculated HF, DFT (6-31+G*) bond length and angle is about 0.079 Å, 0.086 Å (parameter number 20), -6.96° and -7.34° (parameter number 23) respectively. The results can, however, better be represented in graphical form as has been given in Fig. 3. As a result, the optimized bond lengths and angles by DFT method show the best agreement with the experimental values.

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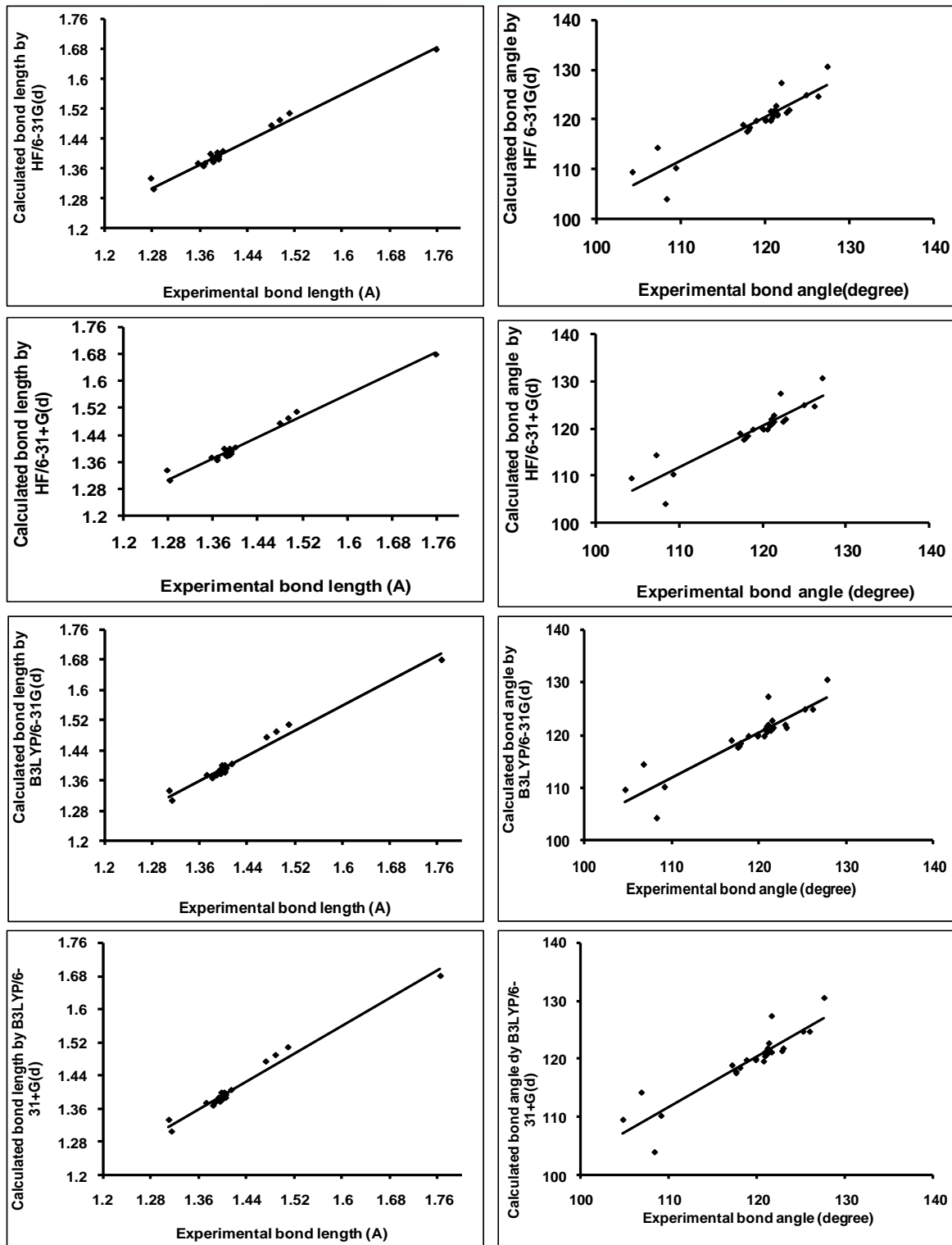


Figure 2. Calculated bond lengths and bond angles in comparison with experimental data

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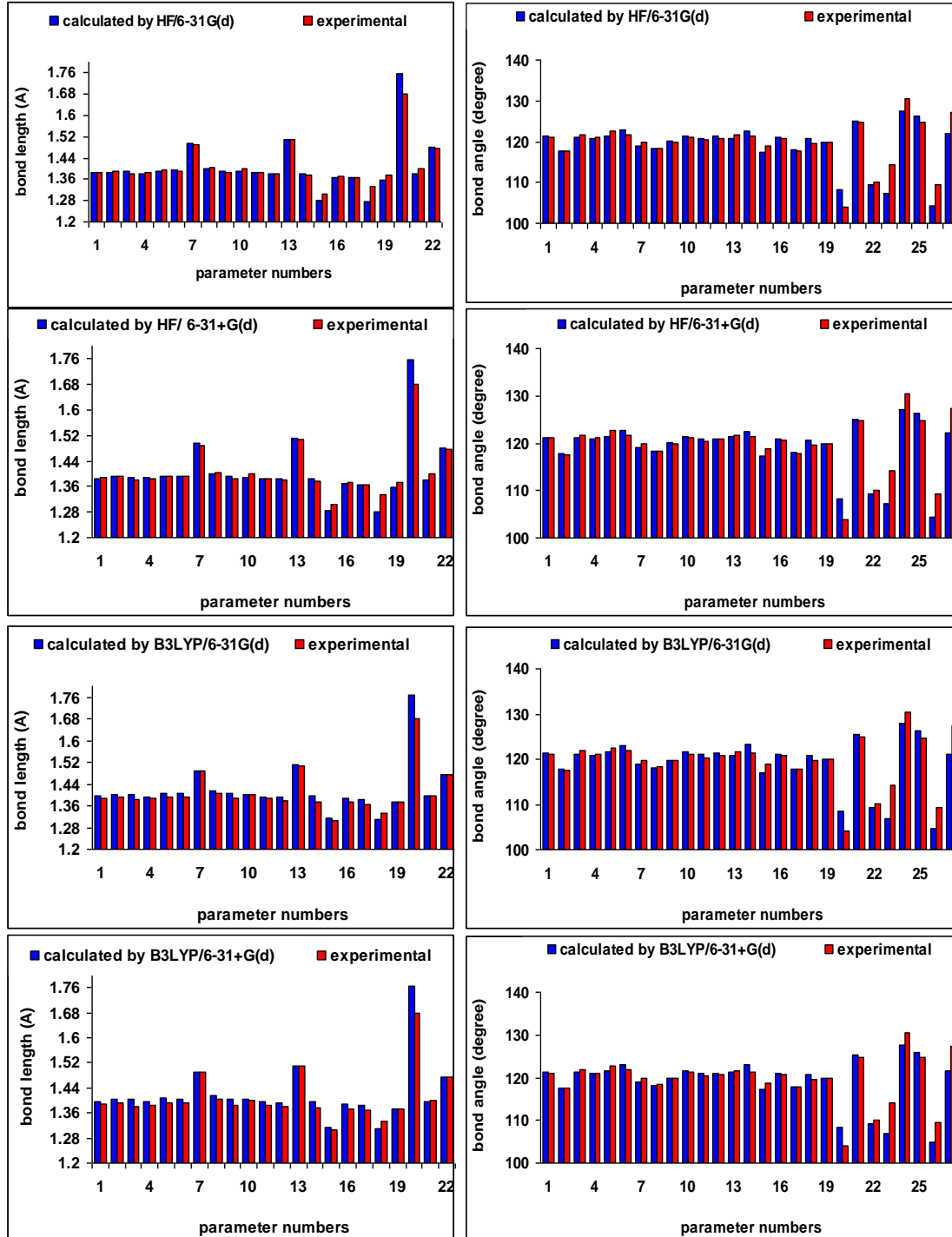


Figure 3. Calculated bond lengths and bond angles in comparison with experimental data

4.2 Vibrational assignments

The literature search has revealed that DFT calculations and vibrational analysis have not been reported so far on 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol. Therefore, we have calculated the theoretical vibrational spectra of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol by using HF and B3LYP, methods with 6-31G (d) basis set. Title compound contains 34 atoms so that, it has 96 normal modes.

Table 2. Calculated wave numbers for 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol using HF/6-31G (d) level a

Num-ber	Assignments	Wave number			IR Inten.	Red mass	Force const.	Raman active
		Unscaled	Scaled					
1	ν_{as} NH2	3848.58	3515.68	15.88	1.10	9.60	40.16	
2	ν_s NH2	3742.23	3418.52	5.710	1.04	8.63	73.08	
3	ν_s ring C-H	3397.34	3103.46	18.66	1.09	7.46	227.37	
4	ν_{as} ring C-H	3386.22	3093.31	9.41	1.09	7.40	140.58	
5	ν_{as} ring C-H	3385.92	3093.04	26.43	1.09	7.39	60.70	
6	ν_{as} ring C-H	3376.29	3084.24	13.86	1.09	7.33	82.80	
7	ν_{as} ring C-H	3374.14	3082.28	15.18	1.09	7.33	95.30	
8	ν_{as} ring C-H	3360.92	3070.20	1.89	1.08	7.23	53.42	
9	ν_{as} ring C-H	3359.79	3069.17	19.11	1.09	7.25	63.73	
10	ν_{as} ring C-H	3347.85	3058.26	21.79	1.08	7.19	83.01	
11	ν_{as} CH ₃	3282.74	2998.78	22.52	1.10	7.00	66.83	
12	ν_{as} CH ₃	3255.49	2973.89	30.88	1.10	6.86	99.75	
13	ν_s CH ₃	3202.05	2925.07	44.39	1.03	6.27	181.83	
14	ν SH	2953.46	2697.98	1.00	1.03	5.33	144.71	
15	Scis. NH2	1857.99	1697.27	52.64	1.14	2.31	10.75	
16	ν ring C=C	1823.28	1665.56	2.66	5.52	10.82	170.32	
17	ν ring C=C	1810.68	1654.05	6.69	5.58	10.79	89.62	
18	ν C=C+ ν C=N	1783.36	1629.10	16.20	7.11	13.33	75.47	
19	ν C=C+ ν C=N	1760.06	1607.82	10.39	5.87	10.71	20.91	
20	ν C=C+ ν C=N	1748.03	1596.82	9.66	5.57	10.04	13.89	
21	ν N27-C29	1703.93	1556.54	77.26	9.42	16.12	41.57	
22	δ ring C-H	1696.71	1549.94	19.60	2.66	4.52	7.23	
23	δ ring C-H	1648.27	1505.69	48.83	2.49	4.00	7.64	
24	Scis. CH2	1638.02	1496.33	14.74	1.13	1.79	15.65	
25	Scis. CH2	1632.85	1491.61	4.89	1.05	1.65	18.65	
26	δ ring C-H+ ν N-N	1626.82	1486.09	37.77	3.91	6.10	13.03	
27	δ ring C-H+ ν N-N	1601.93	1463.36	9.72	2.97	4.50	10.21	
28	δ CH3	1567.75	1432.13	1.76	1.25	1.82	20.32	
29	δ ring C-H	1560.69	1425.69	5.23	2.30	3.30	0.41	
30	ν_{as} C-N-C	1504.64	1374.49	16.05	4.71	6.29	8.44	
31	NH2 Twist.+ δ ring C-H	1464.36	1337.69	2.07	1.29	1.63	0.91	
32	NH2 Twist.+ δ ring C-H	1462.91	1336.36	4.50	1.29	1.62	3.86	
33	δ ring C-H	1428.86	1305.26	1.97	2.04	2.45	13.49	
34	ν C-C Ar.	1410.30	1288.31	0.91	3.76	4.40	0.910	
35	δ ring C-H	1375.44	1256.46	2.54	2.33	2.59	2.54	
36	ν C-C	1326.84	1212.07	1.36	3.27	3.39	1.36	
37	δ ring C-H	1324.74	1210.15	1.31	1.48	1.53	0.20	
38	δ ring C-H	1313.37	1199.77	2.66	1.14	1.16	6.85	
39	ν_{as} C-C-C	1294.57	1182.59	0.32	2.35	2.32	0.81	
40	ν ring N-N	1245.97	1138.19	2.00	2.87	2.62	2.06	

^a Harmonic frequencies (in cm^{-1}), IR intensities (km mol^{-1}), reduced masses (amu) and force constants ($\text{m dyn A}^{\circ-1}$). ν , stretching; δ , in-plane bending; γ , out-of-plane bending; ω , wagging; a, asymmetric, s, symmetric; ρ , rocking; Twist., twisting; Scis., scissoring

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Continue to table 2

Num-ber	Assignments	Wave number		IR Inten.	Red mass	Force const.	Raman active
		Unscaled	Scaled				
41	δ ring C-H	1222.69	1116.93	1.74	2.41	2.12	8.87
42	ν ring C=C	1207.39	1102.95	2.34	3.18	2.73	21.20
43	ν ring C=C	1199.06	1095.34	3.41	1.97	1.67	0.37
44	δ CH ₃	1174.03	1072.47	0.37	1.91	1.55	3.62
45	δ CH ₃	1173.15	1071.67	7.65	2.42	1.96	4.07
46	ν C-S	1147.04	1047.82	4.38	3.52	2.73	28.78
47	ν_s C-C-C	1125.30	1027.96	0.52	2.51	1.87	3.57
48	γ ring C-H	1123.73	1026.52	0.21	1.41	1.05	0.33
49	γ ring C-H	1108.20	1012.34	1.77	1.36	0.98	0.67
50	δ CH ₃ + ring C-C-C	1101.13	1005.88	7.61	3.86	2.76	5.77
51	γ ring C-H+ δ CH ₃	1092.56	998.06	0.63	1.56	1.09	2.28
52	γ ring C-H+ δ CH ₃	1088.51	994.357	1.27	1.50	1.04	2.78
53	γ ring C-H	1085.55	991.65	3.14	1.43	0.99	1.13
54	δ C-N-N+ ring pucker	1074.23	981.31	59.81	5.87	3.99	9.79
55	δ SH	1035.30	945.74	8.97	1.27	0.80	7.16
56	γ ring C-H	1002.19	915.50	2.56	1.43	0.84	3.05
57	ω NH ₂ + δ S-H	993.48	907.55	115.93	1.45	0.84	3.24
58	γ ring C-H	960.58	877.49	1.53	1.24	0.67	3.84
59	γ ring C-H	935.47	854.55	36.39	1.46	0.75	0.19
60	ν C-C + ring pucker.	876.93	801.07	0.76	5.40	2.44	29.65
61	γ ring C-H	869.96	794.70	31.90	1.65	0.74	1.23
62	γ ring C-C-C+C-H	853.581	779.74	33.19	2.53	1.08	2.89
63	γ N-C-N	826.30	754.82	6.40	6.11	2.46	2.88
64	δ ring C-C-C	801.66	732.31	6.90	5.35	2.02	7.86
65	γ C-C-C	800.49	731.24	2.73	3.40	1.28	3.00
66	ν N-N str	778.27	710.95	3.77	6.34	2.26	6.34
67	γ N-C-N	769.87	703.28	6.48	10.56	3.68	2.41
68	δ C-C-C	728.43	665.42	3.78	5.84	1.82	5.77
69	δ C-C-C	702.64	641.86	1.02	6.63	1.92	5.76
70	δ C-N-N+H-S-C	644.46	588.71	13.04	4.52	1.10	1.63
71	γ ring H-C-C	621.44	567.69	7.56	3.23	0.73	0.87
72	δ C-C-C	609.99	557.23	1.73	4.71	1.03	2.32
73	γ C-C-C	591.79	540.60	10.66	3.81	0.78	0.97
74	ν C-S	557.86	509.60	10.66	3.81	0.78	1.22
75	Ring deformation	501.20	457.85	0.28	6.42	1.17	1.66
76	ω NH ₂ + γ C-S-H	467.75	427.29	1.01	4.71	0.69	1.10
77	Ring deformation	460.34	420.52	6.54	4.97	0.64	1.30
78	NH ₂ Twist.	425.44	388.64	0.90	3.02	0.37	3.79
79	γ C-C-CH ₃	389.94	356.21	0.57	4.43	0.47	2.31
80	NH ₂ tow.	364.83	333.27	0.39	3.36	0.30	2.95
81	γ C-C-C	352.61	322.11	68.58	1.23	0.09	5.02
82	γ C-C-C	330.45	301.86	0.66	3.83	0.28	8.28
83	γ C-N-N+S-H	278.79	254.67	9.05	4.25	0.27	0.54
84	γ C-N-N+NH ₂	264.12	241.27	1.23	5.66	0.25	1.64
85	γ C-N-N	253.42	231.50	1.03	5.13	0.21	1.25
86	γ C-N-N+ δ C-S-H	223.64	204.29	2.40	4.32	0.16	1.13
87	δ NH ₂ +C-S-H	215.19	196.58	1.48	4.85	0.14	0.76
88	γ S-H	176.81	161.52	0.60	4.87	0.13	4.19
89	δ NH ₂ +CH ₃	160.14	146.29	16.69	1.12	0.02	1.60
90	γ ring	147.04	134.32	0.39	4.72	0.07	3.25
91	γ ring	106.65	97.428	1.50	5.13	0.03	6.22
92	γ CH ₃ + ring	91.164	83.278	0.54	4.68	0.02	0.34
93	γ ring	82.26	75.152	0.35	4.89	0.01	4.23
94	γ CH ₃ + ring	63.40	57.920	1.99	4.36	0.01	6.24
95	δ ring	41.09	37.544	2.51	5.37	0.00	3.13
96	ρ CH ₃	37.75	34.487	0.60	6.44	0.00	0.38

Table 2 show the vibrational frequencies and assignments of the vibrational frequencies (cm^{-1}) of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol. To our knowledge, there is no complete, assigned, experimental vibrational spectrum of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol there exists no information at all. However, several modes for title compound have been assigned and experimental frequencies measured [11]. The vibrational bands assignments have been made by using both the animation option of GaussView 3.0 graphical interface for gaussian programs. The frequency values computed at these levels contain known systematic errors. Therefore, we have used the scaling factor values of 0.9135, 0.9163 and 0.9806 for HF/6-31G*, 6-31+G* and B3LYP/6-31G*, respectively. All quoted vibrational frequencies reported along the paper are thus scaled values. Frequency changes well reflect the geometry changes.

The simulated scaled and unscaled IR and Raman spectrum obtained from HF/6-31G* is presented in Fig. 4. From the calculated frequencies the higher intensities correspond NH₂ wagging, N27-C29 stretching. The strongest bands at 1703.93 cm^{-1} have been assigned to the C=N stretching groups modes. Raman ring C-H symmetry, asymmetry stretching and the symmetrical stretching in CH₃ (CH₃ sym. stretch) modes have dominate intensities.

4.2a C-NH₂ vibrations: The molecule under investigation possesses only one NH₂ group and hence one expects one symmetric and one asymmetric N-H stretching vibrations in NH₂ group. In all the primary aromatic amines, the N-H stretching frequency occurs in the region 3300–3500 cm^{-1} [19]. Hence, the weak bands in IR spectrum were located at 3515.68 and 3418.52 cm^{-1} assigned to N-H asymmetric and symmetric stretching vibrations, respectively in NH₂ group. The computed -NH₂ scissoring vibration at 1697.27 cm^{-1} in HF/6-31G* is in agreement with the expected experimental value.

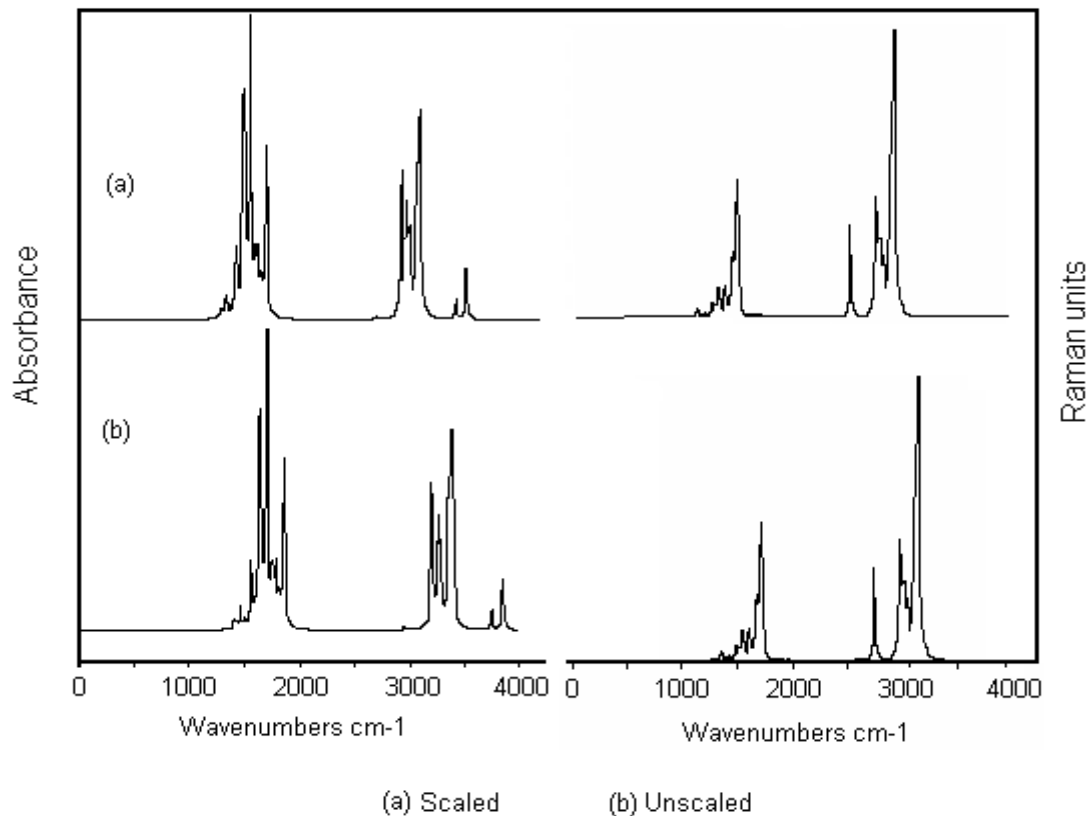


Figure 4. Comparison of a) scaled and b) unscaled computed IR and Raman spectra of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol at HF/6-31G (d) level

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4.2b Methyl group vibrations: The title compound 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol, possesses one CH₃ group attached to the benzene ring. There are nine fundamentals one can expect to CH₃ group, namely the symmetrical stretching in CH₃ (CH₃ sym. stretch) and asymmetrical stretching (in plane hydrogen stretching mode); the symmetrical (CH₃ sym. deform) and asymmetrical (CH₃ asym. deform) deformation modes; the in-plane rocking, out-of-plane rocking, twisting and bending modes. For the methyl compounds, the stretching mode appears in the range of 2825–2870 cm⁻¹, lower in magnitude compared to its value in CH₃ compounds (2860–2935 cm⁻¹), whereas the two asymmetric modes for both the types of compounds lie in the same region of 2998–2925 cm⁻¹. The FTIR bands at 2998 and 2925 cm⁻¹ and FT-Raman band at 2851 and 2739 cm⁻¹ represent the asymmetric and symmetric CH₃ stretching vibrations of the methyl group of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol.

4.2c C=N, C–N vibrations: The identification of C–N vibrations is a difficult task, since the mixing of vibrations is possible in this region. However, by using both the animation option of GaussView 3.0 graphical interface for gaussian programs the C–N vibrations identified. Silverstein [19] assigned C–N stretching absorption in the region 1382–1266 cm⁻¹ for aromatic amines. The IR bands appearing at 1510 and 1441 cm⁻¹ are assigned to νC=N vibrations and 1374 and 1209 cm⁻¹ are assigned to νC–N vibrations with the δCH for the title compound.

4.2d C–S, S–H vibrations: The IR bands appearing at 2697.98 and 1047.82 cm⁻¹ are assigned to νS–H vibrations and 945.74 and 161.52 cm⁻¹ are assigned to S–H in plane bending vibrations with the out plane for the title compound.

4.3. VCD Spectra

Vibrational Circular Dichroism (VCD) spectroscopy in the Near Infrared (NIR) range was successfully tried long time ago [20], in one case even earlier than the more known and used VCD spectroscopy in the IR range. More recently some advancement has been achieved in developing new instrumentation, based either on dispersive or Fourier transform interferometric technologies [21, 22]. The usability of the NIR-VCD data needs though a parallel advancement in the interpretation of the spectra. Such an interpretation is hampered by many factors, among which two are of utmost importance: the enormous number of modes that may in principle contribute to the overtone regions and the essential role played by anharmonic terms in determining both the wave functions and the functional form of the electric and magnetic dipole moment operators. Necessarily one has to resort to some kind of approximations. The optical activity of asymmetric molecules is explained when a plane polarized radiation passes through an active medium. The plane of the emergent plane polarized radiation rotates by an angle. The plane polarized beam can be considered as a superposition of two oppositely rotating circularly polarized component. The absorbance coefficient is defined as, $\Delta\epsilon = \epsilon_R - \epsilon_L$ [23]. Simulated VCD and absorption spectra of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol are plotted in Fig. 5. These simulations were obtained with HF/6-31G (d) level calculation.

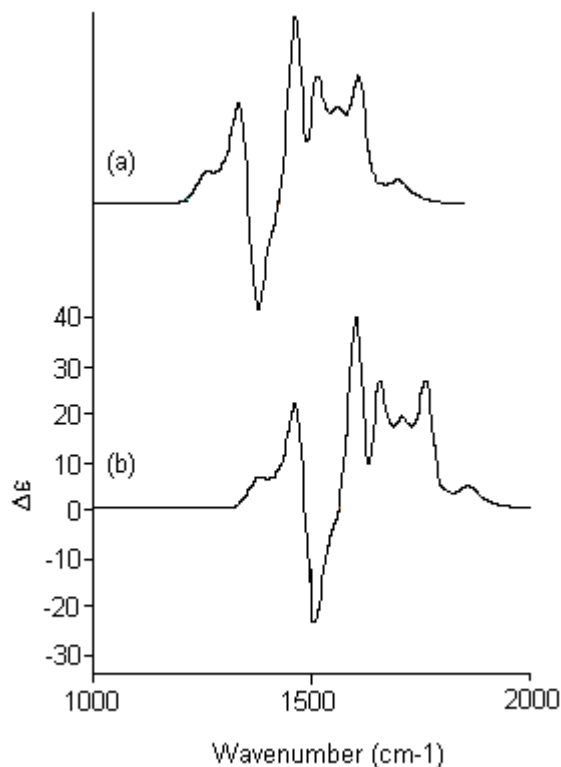


Figure 5. Comparison of a) scaled and b) unscaled computed VCD spectra of the 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol at HF/6-31G(d) level

4.4 ^1H and ^{13}C NMR

NMR spectra were recorded on a Shimadzu AMX400, spectrometer by using CDCl_3 as solvent and TMS as an internal standard (Chemical shift in ppm). Tables 3 and 4 give the calculated NMR chemical shifts at HF and B3LYP/6-31G(d) levels of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol after subtraction of the value of tetramethylsilane calculated at the same level of theory. The first peak can be attributed unambiguously to the methyl group (C21) at 20.4-21.8 ppm while at last signal correspond to carbon atom linked to Nitrogen atoms at the five member ring. One can reasonably ascribe the signal at 146.5 ppm to C29 and that at 132.0 ppm to C14 calculated by HF/6-31G(d) level and basis set. However, Ab initio calculations of the ^{13}C NMR chemical shifts, as implemented in commercial softwares such as Gaussian, can not only prove the above attribution but also give additional information on the structure of the organic moiety and lead to a more precise location of light nuclei such as hydrogen atoms.

Table 3. Calculated (HF/6-31G*) and experimental ^1H chemical shifts (ppm from TMS, $\delta_{\text{TMS}} = 0.00$) for 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol

Atomic specific	^1H chemical shifts		Expt.[11]
	HF/6-31G(d)	B3LYP/6-31G(d)	
H1: 34, 23	1.96, 2.04	1.88, 2.01	
H2: 22, 24, 33	2.44, 2.50, 2.62	2.38, 2.48, 2.92	
H3: 32	3.82	3.81	
H4: 7, 8	7.22, 7.21	6.66, 6.88	7.73-7.78
H5: 9, 16, 20	7.55, 7.64, 7.70	7.21, 7.28, 7.29	7.92-7.98
H6: 10, 19, 18	7.83, 7.86, 7.96	7.46, 7.41, 7.62	8.1

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Table 4. Calculated (HF/6-31G*) ¹³C NMR chemical shifts (ppm from TMS, $\delta_{TMS} = 0.00$) for 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol

Atomic specific	¹³ C chemical shifts	
	HF/6-31G(d)	B3LYP/6-31G(d)
C1: C25	154.5	151.0
C2: C29	146.5	144.8
C3: C11	142.6	137.1
C4: C6	136.3	134.2
C5: C3	134.8	130.0
C6: C14	132.0	126.5
C7: C2	148.382	146.702 (140.69)
C8: C1,2,4,5,15,13,17	129.4, 126.4, 126.0, 129.0, 129.1, 127.8, 124.4	122.8, 122.5, 122.7, 122.9, 122.9, 123.5, 120.2
C9: C21	20.4	21.8

4.5 Mulliken and natural bond orbital (NBO) charges

To clarify the nature of the molecular structure, the NBO analysis was carried out. Atomic charges were obtained from Mulliken and natural bond orbital (NBO) analysis [24], as implemented in Gaussian 03W. Table 5 gives the Mulliken effective atomic charges and natural atomic charges (q) for structure of the title compound calculated with the HF and B3LYP methods and 6-31G (d) and 6-31+G (d) basis set.

Table 5. Mulliken atomic charges of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol for different levels and basis sets.

Atom with numbering	Mulliken				NBO	
	6-31G(d)	HF 6-31+G(d)	6-31G(d)	B3LYP 6-31+G(d)	HF 6-31G(d)	B3LYP 6-31G(d)
C1	-0.2056	-0.5030	-0.1766	-0.4384	-0.197	-0.220
C2	-0.2348	-0.2997	-0.1946	-0.1021	-0.225	-0.231
C3	0.0403	0.4483	0.1776	0.2959	-0.029	-0.044
C4	-0.2328	-0.6011	0.1920	-0.4509	-0.232	-0.238
C5	-0.2042	-0.5913	-0.1677	-0.5665	-0.202	-0.219
C6	-0.0316	0.4972	0.0484	0.4316	-0.075	-0.071
C11	0.0367	0.1004	0.0857	0.1236	-0.006	-0.019
C12	0.0017	0.1860	0.1001	-0.0402	-0.092	-0.086
C13	-0.2223	-0.2911	-0.1887	-0.0807	-0.217	-0.221
C14	-0.1845	-0.0698	-0.1586	-0.1211	-0.174	-0.192
C15	-0.1876	-0.2441	-0.1217	-0.0900	-0.203	-0.226
C17	-0.2096	-0.3063	-0.1348	-0.1486	-0.232	-0.239
C21	-0.5072	-0.7407	-0.5302	-0.8303	-0.641	-0.699
C25	0.5135	-0.3270	0.3843	-0.6821	0.442	0.362
C29	0.3234	0.2355	0.2675	0.2809	0.267	0.182
N26	-0.3791	-0.0441	-0.3600	0.0121	-0.340	-0.294
N27	-0.3545	-0.1708	-0.3177	-0.2051	-0.373	-0.333
N28	-0.5397	0.3420	-0.3728	0.4917	-0.320	-0.279
S30	0.3235	-0.0615	-0.0301	0.0565	0.025	0.023
H7	0.2391	0.2677	0.1618	0.2158	0.245	0.257
H8	0.2049	0.2339	0.1312	0.1803	0.229	0.243
H9	0.1980	0.2321	0.1246	0.1760	0.225	0.240
H10	0.2118	0.2422	0.1355	0.1885	0.233	0.246
H16	0.2131	0.2445	0.1371	0.1901	0.234	0.246
H18	0.2318	0.2651	0.1561	0.2115	0.243	0.258
H19	0.2072	0.2384	0.1340	0.1829	0.230	0.245
H20	0.2082	0.2402	0.1359	0.1854	0.232	0.246
H22	0.1775	0.2188	0.1623	0.2292	0.227	0.253
H23	0.1780	0.2037	0.1597	0.2155	0.224	0.247
H24	0.1783	0.1978	0.1631	0.2061	0.228	0.243
H32	0.1490	0.1377	0.1479	0.1456	0.163	0.189
H33	0.3816	0.4523	0.3436	0.4296	0.391	0.408
H34	0.3877	0.4636	0.3512	0.4439	0.397	0.412

The results of NBO analysis allow many of the quantitative trends in molecular structure, stability and spectroscopic properties to be rationalized in terms of non-pair wise-additive charge transfer delocalization between monomers. Our interest here is in the comparison of different methods to describe the electron distribution in 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol as broadly as possible, and assess the sensitivity of the calculated charges to changes in (i) the choice of the basis set; (ii) the choice of the quantum mechanical method. Mulliken charges, calculated by determining the electron population of each atom as defined in the basis functions. The results can, however, better be represented in graphical form as has been given in fig. 6. From these results, it will be possible to say to the change to charge distribution by a change in basis set. The charges depending on basis set and are changed due to polarization. The calculated results of NBO analysis using the HF and B3LYP methods with the 6-31G (d) basis set indicate all nitrogen and carbon atoms in title compound have negative charge (except C25 and C29). Although the Mulliken analysis cannot predict exactly the atomic charges quantitatively, the sign of atomic charge is correct [25].

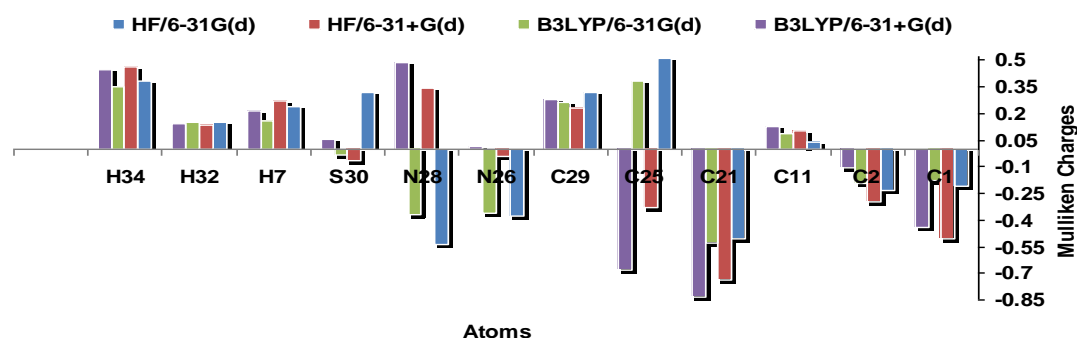


Figure 6. Comparison of different methods for calculated Mulliken atomic charges.

4.6 Thermodynamic properties

The calculated thermodynamic parameters are presented in Table 6. Scale factors have been recommended [26] for an accurate prediction in determining the zero-point vibrational energies. The variation in the thermodynamic parameters seems to be insignificant.

Table 6. Calculated dipole moments (D. Mom), zero-point vibrational energy (ZPV) (kcal/mol), thermal energy (E thermal; kcal/mol) and Rotational constants (GHZ) for 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol definitions of theory levels

Theory levels	D. Mom	ZPV	E			
			(Thermal)	Rotational constants		
HF/6-31G(d)	4.867	178.77	188.764	0.331	0.323	0.187
B3LYP/6-31G(d)	4.708	166.08	176.783	0.329	0.322	0.184

5. Conclusions

The results of the study lead to the following conclusions:

- (i) The ground state geometries were optimized using the HF and B3LYP methods with the 6-31G (d), 6-31+G (d) basis set and geometries reported within the limits of accuracy of available experimental data. The bond lengths and angles calculated for title compound show quite good agreement with experimental values. The agreement for bond angles is not as good as that for the bond distances.
- (ii) The frequency assignments performed for the first time from FTIR and FT-Raman spectra recorded were for 2-(4-methyl-2-biphenyl)-4-amino-1,2,4-triazole-3-thiol.
- (iii) Mulliken charges of dacarbazine at different levels were calculated and the results discussed.
- (iv) calculated NMR chemical shifts and thermodynamic properties at HF and B3LYP/6-31G(d) levels of 2-(4-methyl-2-biphenyl)-4-amino-1, 2, 4-triazole-3-thiol were discussed and reported.

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