



Optimization and Vibrational Study of 2-propylpyridine-4-carbothioamide by DFT- A theoretical study

K. Rajalakshmi^{1*}, M.Vetrivel²

¹Department of Physics, SCSVMV, Kanchipuram– 631 561, India

²Department of Mechanical Engineering, SCSVMV, Kanchipuram– 631 561, India

Abstract: The molecular structure and simulated vibrational spectra of 2-propylpyridine -4-carbothioamide have been calculated using the different density functional theoretical methods. The comparative performance of different DFT methods at various basis sets has been examined and predicted molecular structure and vibrational spectra of the molecule. The calculated results show that DFT/B3LYP functional and 6-31 G basis set gives the highest certainty in predicting the structure and vibrational spectra of 2-propylpyridine -4-carbothioamide.

Keywords: 2-propylpyridine-4-carbothioamide, DFT, molecular structure, vibrational spectra.

1. Introduction

2-propylpyridine-4-carbothioamide (2P4C) is a drug used in the treatment of tuberculosis and in the treatment of leprosy. It is considered as a second-line drugs for tuberculosis as the number of drug resistant tuberculosis cases continues to rise. The burden of tuberculosis (TB) is major impediment to improved health for the world's population [1- 2]. It is rapidly and widely distributed into body tissues and is extensively metabolized to active and inactive metabolites and it is an efficacious drug for the treatment of multidrug-resistant tuberculosis [3].

Several recent studies [4-7] have shown that Density functional theory DFT can yield reasonable vibrational frequencies and geometries and it is much superior to the conventional methods. Therefore, the DFT method was chosen as the basic method in the present study for calculating the geometries and vibrational frequencies of 2-propylpyridine-4-carbothioamide.

The aim of this paper is to compare the calculated results with the experimental data of 2-propylpyridine-4-carbothioamide and then to find effective DFT method that would offer a higher certainty of predicting geometry and vibrational spectra of 2-propylpyridine-4-carbothioamide.

2. Theoretical Calculations

The entire quantum chemical calculations have been performed at DFT with various basis sets using the Gaussian 09W program [8]. The molecular geometry optimizations were carried out by DFT using B3LYP, B3PW91, HCTH, SVWN, mPW1PW91 and PBEPBE [9-10] functional and different basis sets including LANL2DZ, SDD, LANL2MB, 6-31G, 6-311G, 3-21G. Based on the optimized structures, harmonic frequency calculations of the title molecule were calculated at the same level of theory. The wave number-linear scaling

(WLS) method which is a general and simple scaling procedure [11-12] was applied to correct the calculated harmonic frequencies.

3. Results and discussion

3.1 Geometry optimization with various methods at Aug-CC-pVDZ basis set

The DFT methods employed in the present paper are representative in aspect of the exchange–correlation energy and were commonly used in numerous theoretical studies.

B3LYP, B3PW91 and mPW1PW91 are classified to hybrid Hartree–Fock density-functional theory (hybrid-DFT) which combines the exchange–correlation of a percentage of Hartree–Fock (or exact) exchange. HCTH and PBEPBE are classified to the generalized gradient approximation (GGA) which makes the exchange and correlation energies dependent not only on the density but also on the gradient of the density give better total energies, atomization energies and structural energy differences and tend to expand and soften bonds compensating for the SVWN tendency to over bind. SVWN is the older local-spin-density approximation (LSDA) suitable for systems having slowly varying densities, but it typically overestimate binding energies and overly favor high spin-spin state structures [13-17].

Fig. 1 presents the optimized structure of 2-propylpyridine-4-carbothioamide at DFT/B3LYP/6-31 G method. The optimized geometrical parameters determined with different DFT methods at Aug-CC-pVDZ functional for the title molecule and the experimental data are collected in Table 1.

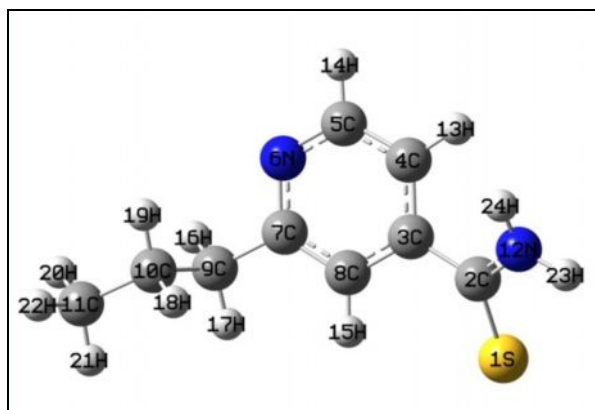


Fig. 1. Optimized structure of 2-propylpyridine-4-carbothioamide at DFT/B3LYP/6-31 G method

Table 1. Comparison of bond length (Å) and bond angles (°) calculated with various DFT methods for 2-propylpyridine-4-carbothioamide

Geometry	Description	Aug-CC-pVDZ					
		PBEPBE	SVWN	HCTH	B3LYP	mPW1PW91	B3PW91
BOND LENGTH							
R(1,2)	1.7120	1.6912	1.6738	1.6620	1.6774	1.6869	1.6634
R(2,3)	1.4786	1.4957	1.4768	1.4915	1.4889	1.4946	1.4902
R(2,12)	1.3479	1.3450	1.3314	1.3520	1.3300	1.3366	1.3488
R(3,4)	1.3995	1.4101	1.3968	1.4033	1.398	1.4030	1.4010
R(3,8)	1.3991	1.4067	1.3937	1.3998	1.3948	1.3997	1.3972
R(4,5)	1.3806	1.4023	1.3911	1.3954	1.3920	1.3960	1.3945
R(4,13)	1.0800	1.0973	1.0997	1.0904	1.0879	1.0887	1.0902
R(5,6)	1.3186	1.3471	1.3324	1.3347	1.3320	1.3391	1.3333
R(5,14)	1.0800	1.1007	1.1024	1.0946	1.0909	1.0920	1.0933
R(6,7)	1.3183	1.3577	1.3429	1.3471	1.3430	1.3484	1.3445
R(7,8)	1.3811	1.4073	1.3938	1.4007	1.3970	1.4013	1.3986
R(7,9)	1.5070	1.5100	1.4875	1.5060	1.5022	1.5090	1.5047

R(8,15)	1.0800	1.0974	1.1010	1.0893	1.0877	1.0882	1.0894
R(9,10)	1.5300	1.5435	1.5199	1.5352	1.5326	1.5411	1.5349
R(9,16)	1.0901	1.1075	1.1100	1.0992	1.0982	1.0994	1.0998
R(9,17)	1.0900	1.1071	1.1087	1.0992	1.0979	1.0992	1.0997
R(10,11)	1.5300	1.5319	1.5100	1.5238	1.5227	1.5307	1.5251
R(10,18)	1.0900	1.1085	1.1103	1.1010	1.0995	1.1007	1.1013
R(10,19)	1.0900	1.108	1.1100	1.0994	1.0988	1.1000	1.0998
R(11,20)	1.0900	1.1073	1.1084	1.0992	1.0983	1.1000	1.0998
R(11,21)	1.0900	1.1073	1.1084	1.0995	1.0983	1.1000	1.1000
R(11,22)	1.0900	1.1061	1.1064	1.0983	1.0971	1.0989	1.0987
R(12,23)	0.9700	1.0191	1.0219	1.0087	1.0095	1.0118	1.0100
R(12,24)	0.9700	1.0200	1.0232	1.0090	1.0100	1.0122	1.0101
Mean Absolute Deviation		0.01956	0.01984	0.01420	0.01303	0.01406	0.01379
BOND ANGLE							
A(1,2,3)	120.0022	122.0070	121.8350	122.7556	121.8481	122.1086	122.8338
A(1,2,12)	119.9995	122.3261	122.5036	122.1886	122.5901	122.3272	122.1628
A(3,2,12)	119.9977	115.6544	115.6551	115.026	115.5511	115.5517	114.9876
A(2,3,4)	120.9356	121.4780	121.5038	121.7166	121.2085	121.1790	121.7285
A(2,3,8)	120.9279	120.7497	120.5266	120.8728	120.6659	120.8741	120.5114
A(4,3,8)	118.1359	117.7699	117.9692	117.4048	118.1230	117.9441	117.7585
A(3,4,5)	118.9933	118.3791	118.3564	118.4831	118.1597	118.3159	118.3801
A(3,4,13)	120.4997	121.9647	122.0904	121.7112	122.0007	121.9538	121.8157
A(5,4,13)	120.4997	119.6024	119.4887	119.7344	119.7909	119.6852	119.7280
A(4,5,6)	120.9065	124.0897	123.6848	124.185	123.8903	123.8186	123.9366
A(4,5,14)	119.5414	119.6389	119.6828	119.7459	119.6941	119.728	119.8852
A(6,5,14)	119.5520	116.2702	116.6311	116.0678	116.4147	116.4526	116.1769
A(5,6,7)	122.0705	117.7767	118.3227	117.8022	118.2323	118.2493	118.0524
A(6,7,8)	120.9041	122.0380	121.8828	122.0581	121.9121	121.8234	122.0904
A(6,7,9)	119.5480	116.8001	116.6887	116.6024	116.9476	117.0372	116.4806
A(8,7,9)	119.5473	121.1390	121.3846	121.3286	121.1215	121.1233	121.4135
A(3,8,7)	118.9871	119.9372	119.7777	120.0534	119.6711	119.8375	119.7711
A(3,8,15)	120.5048	119.5655	119.0800	119.301	119.834	119.8855	119.2405
A(7,8,15)	120.5056	120.4972	121.1419	120.6446	120.4946	120.2766	120.9879
A(7,9,10)	109.4751	112.1184	111.2581	112.9877	112.176	112.4543	112.215
A(7,9,16)	109.4729	108.6061	108.8281	108.0864	108.5257	108.5550	108.2251
A(7,9,17)	109.4731	109.6273	109.9645	109.5792	109.5635	109.4932	109.6648
A(10,9,16)	109.4675	109.1588	108.9692	109.0538	109.2938	109.1996	109.1345
A(10,9,17)	109.4713	109.3605	109.8608	109.4815	109.4652	109.2821	109.7648
A(16,9,17)	109.4675	107.8719	107.8837	107.4945	107.7088	107.7417	107.7193
A(9,10,11)	109.4739	112.4040	112.0752	113.1884	112.4843	112.4932	112.6505
A(9,10,18)	109.4670	108.9664	108.9427	109.0543	109.0055	109.0031	109.0700
A(9,10,19)	109.4670	108.7307	108.2228	108.5757	108.7794	108.8356	108.4292
A(11,10,18)	109.4672	109.9339	110.4364	109.6319	109.8698	109.7943	109.8628
A(11,10,19)	109.4736	110.0295	110.6288	109.8061	109.9624	109.8800	110.0847
A(18,10,19)	109.4698	106.5966	106.339	106.3492	106.5550	106.6570	106.5460
A(10,11,20)	109.4672	111.0451	110.8191	111.3301	111.0444	111.0335	111.0859
A(10,11,21)	109.4736	111.1523	111.051	111.5764	111.133	111.1157	111.3545
A(10,11,22)	109.4712	111.131	111.7379	111.0779	111.0729	110.997	111.1473
A(20,11,21)	109.4698	107.7212	107.4495	107.5551	107.7652	107.8182	107.6611
A(20,11,22)	109.4668	107.8295	107.8374	107.5684	107.8481	107.8727	107.7248
A(21,11,22)	109.4786	107.8026	107.7657	107.5325	107.8227	107.8551	107.6926
A(2,12,23)	119.9955	119.7068	119.5234	118.5827	119.844	119.8933	118.4352
A(2,12,24)	119.9969	121.9620	121.7206	121.7444	121.8599	122.0283	121.5266

A(23,12,24)	120.0076	118.0916	118.5373	118.6139	118.1464	117.9346	118.9055
Mean Absolute Deviation	1.4714	1.5102	1.6354	1.4117	1.4152	1.4152	1.5877

It is clear from the table that, B3LYP functional predicts the R(2-3), R(3-4), R(4-13), R(5-6), R(5-14), R(7-8), R(8-15), R(9-10), R(9-16), R(9-17), R(10-18), R(10-19), R(11-20), R(11-21), R(11-22), R(12-23), R(12-24), bond lengths in better agreement with experimental geometries than other methods. The calculated bond angles of various DFT functional differ by 2° with the experimental values. From the results, it is clear that the bond angles obtained from B3LYP functional values matches with the experimental results and this helps in the prediction of bond angle and very similar to the crystal structure of 2-propylpyridine-4-carbothioamide.

3.2 Geometry optimization with B3LYP at various basis sets

In an effort to better evaluate the limit performance and to determine basis set dependence, calculations for optimized geometries with B3LYP functional using various basis sets have been carried out. The calculated geometry parameters with B3LYP at different basis sets were compared with the experimental parameters in Table 2. It is clear that the calculated bond lengths at 6-31G basis sets are in better agreement with the experimental geometry. The calculated bond angles with B3LYP method at various basis sets differs from 2°-4° with the experimental values. These results indicate that the calculated angles with B3LYP/ 6-31G method at various basis sets are very similar to the crystal structure of 2-propylpyridine-4-carbothioamide.

Table 2. Comparison of bond length (in Å) and bond angles (in deg) calculated for 2-propylpyridine-4-carbothioamide with B3LYP methods

Geometry	Description	LANL2DZ	SDD	LANL2MB	6-31G	6-311G	3-21G
		B3LYP					
		BOND LENGTH					
R(1,2)	1.7120	1.7156	1.7063	1.81	1.7105	1.714	1.7156
R(2,3)	1.4786	1.4956	1.4961	1.5116	1.487	1.488	1.488
R(2,12)	1.3479	1.3667	1.3672	1.3708	1.3513	1.3463	1.3532
R(3,4)	1.3995	1.4156	1.4156	1.4196	1.4053	1.4039	1.408
R(3,8)	1.3991	1.4103	1.4104	1.4156	1.4012	1.4005	1.4041
R(4,5)	1.3806	1.4059	1.4062	1.4074	1.3939	1.394	1.3968
R(4,13)	1.0800	1.0864	1.0863	1.0977	1.0812	1.0831	1.0847
R(5,6)	1.3186	1.3534	1.3535	1.3891	1.3472	1.3463	1.3477
R(5,14)	1.0800	1.0874	1.0874	1.1032	1.0817	1.0849	1.0853
R(6,7)	1.3183	1.3658	1.366	1.3989	1.3596	1.3573	1.3603
R(7,8)	1.3811	1.41	1.4102	1.4145	1.3985	1.3957	1.401
R(7,9)	1.5070	1.5134	1.5135	1.5444	1.5066	1.513	1.5088
R(8,15)	1.0800	1.0849	1.0848	1.0991	1.0797	1.0817	1.0833
R(9,10)	1.5300	1.553	1.5531	1.5672	1.5462	1.551	1.5477
R(9,16)	1.0901	1.0977	1.0977	1.1034	1.0928	1.0974	1.0977
R(9,17)	1.0900	1.0983	1.0983	1.1037	1.093	1.0953	1.0971
R(10,11)	1.5300	1.5421	1.5421	1.5554	1.5346	1.542	1.5359
R(10,18)	1.0900	1.1003	1.1003	1.1042	1.0947	1.0971	1.0992
R(10,19)	1.0900	1.0982	1.0983	1.1039	1.0926	1.0953	1.0972
R(11,20)	1.0900	1.0985	1.0985	1.1007	1.0927	1.0964	1.0971
R(11,21)	1.0900	1.0988	1.0988	1.1008	1.0931	1.0965	1.0974
R(11,22)	1.0900	1.0978	1.0978	1.1008	1.0918	1.0955	1.096
R(12,23)	0.9700	1.0128	1.0127	1.0422	1.0063	1.0161	1.0096
R(12,24)	0.9700	1.0127	1.0126	1.0428	1.0069	1.016	1.0099
Mean Absolute Deviation	0.01702	0.01718	0.03310	0.01000	0.01241	0.01287	0.01287
BOND ANGLE							

A(1,2,3)	120.0022	123.1509	123.0614	123.6551	122.1145	122.953	122.9051
A(1,2,12)	119.9995	121.3752	121.4701	119.1798	121.842	121.6653	121.3296
A(3,2,12)	119.9977	115.4679	115.4629	117.1646	116.0416	115.3744	115.761
A(2,3,4)	120.9356	121.5038	121.595	122.4752	121.2874	121.0984	121.4263
A(2,3,8)	120.9279	120.6949	120.6142	119.8709	120.6305	120.9547	120.7077
A(4,3,8)	118.1359	117.7978	117.788	117.6526	118.0813	117.9438	117.8645
A(3,4,5)	118.9933	118.6849	118.6884	118.8105	118.6545	118.7895	118.7589
A(3,4,13)	120.4997	121.8584	121.8696	121.889	121.3192	121.3001	121.4513
A(5,4,13)	120.4997	119.3801	119.3661	119.269	119.9626	119.8411	119.7198
A(4,5,6)	120.9065	123.4105	123.4202	125.5103	123.3291	123.1839	123.2915
A(4,5,14)	119.5414	120.5319	120.5265	119.451	120.1151	120.8805	120.6013
A(6,5,14)	119.552	116.0554	116.0513	115.0382	116.5546	115.9336	116.1056
A(5,6,7)	122.0705	118.4321	118.4156	114.2544	118.26	118.5769	118.4916
A(6,7,8)	120.9041	121.5584	121.5635	123.6559	121.8677	121.43	121.5554
A(6,7,9)	119.5480	116.4385	116.4353	115.5166	116.2131	116.1959	116.3000
A(8,7,9)	119.5473	121.992	121.9904	120.8158	121.907	122.3644	122.1339
A(3,8,7)	118.9871	120.1088	120.1167	120.1124	119.7956	120.0651	120.0289
A(3,8,15)	120.5048	119.3995	119.3624	118.8454	119.1963	119.3818	119.2705
A(7,8,15)	120.5056	120.4903	120.5197	121.0409	121.0076	120.5527	120.7003
A(7,9,10)	109.4751	112.1736	112.1817	111.6942	111.218	112.5391	112.591
A(7,9,16)	109.4729	108.5663	108.5731	108.4808	108.4361	108.3054	108.4459
A(7,9,17)	109.4731	110.0831	110.0754	109.3258	110.086	109.9389	109.8738
A(10,9,16)	109.4675	108.5793	108.5842	109.2218	108.4127	108.6323	108.5202
A(10,9,17)	109.4713	109.4508	109.444	109.5095	110.2835	109.7548	109.7728
A(16,9,17)	109.4675	107.8766	107.8711	108.5486	108.3222	107.5239	107.4874
A(9,10,11)	109.4739	112.1752	112.1935	111.8092	111.9826	112.6319	112.4704
A(9,10,18)	109.467	109.324	109.3199	109.2125	109.0897	109.1933	109.206
A(9,10,19)	109.467	108.4586	108.4631	108.8465	107.4274	108.1866	108.1577
A(11,10,18)	109.4672	109.7496	109.7462	109.5954	109.9435	109.7862	109.8213
A(11,10,19)	109.4736	110.0311	110.0256	109.687	110.5423	110.1216	110.2248
A(18,10,19)	109.4698	106.9548	106.9437	107.5919	107.7277	106.7349	106.7838
A(10,11,20)	109.4672	110.9295	110.9327	110.6492	110.5358	111.0623	111.0224
A(10,11,21)	109.4736	111.2018	111.205	110.6982	110.8351	111.357	111.2798
A(10,11,22)	109.4712	111.1085	111.1098	110.3366	110.8217	111.1099	111.1543
A(20,11,21)	109.4698	107.7893	107.7844	108.3509	108.1636	107.7025	107.6945
A(20,11,22)	109.4668	107.8405	107.839	108.3757	108.213	107.7314	107.7811
A(21,11,22)	109.4786	107.8173	107.8154	108.3515	108.1714	107.7064	107.7421
A(2,12,23)	119.9955	118.8079	118.7586	118.4912	118.7448	119.0702	118.8983
A(2,12,24)	119.9969	122.0811	122.092	122.6236	121.8138	121.9943	122.1334
A(23,12,24)	120.0076	118.8015	118.8081	118.6807	119.0111	118.6665	118.716
Mean Absolute Deviation	1.50642	1.51597	1.59106	1.39303	1.54464	1.54357	

3.3 Vibrational spectra calculated with various methods at Aug-CC-pVDZ basis set

The computed vibrational frequencies (scaled values) and their relative IR intensities of 2-propylpyridine-4-carbothioamide with various DFT methods using Aug-CC-pVDZ basis set are listed in Table 3. In order to reduce the errors in the predictions, several authors proposed different scaling procedures for DFT calculations. The wavenumber-linear scaling (WLS) method, which is based on the linear relationship between the scale factor and calculated harmonic frequencies, is an effective and simple scaling procedure to correct the calculated harmonic frequencies [18-19].

Table 3 Scaled frequencies^a (cm⁻¹) and infrared intensities^b (km/mol) calculated for 2-propylpyridine-4-carbothioamide with various density functional methods using Aug-CC-pVDZ basis set.

Mode	Assignment	Description	Aug-CC-pVDZ					
			B3LYP	B3PW91	HCTH	SVWN	mPW1PW91	PBEPBE
66	$\nu_{as}(\text{NH}_2)$	3500	3695	3713	3692	3750	3756	3635
65	$\nu_s(\text{NH}_2)$	3400	3635	3678	3548	3630	3525	3575
64	$\nu(\text{C-H})$	3200	3220	3250	3194	3126	3234	3235
53	$\delta(\text{ring})$	1650	1627	1652	1570	1628	1666	1578
46	$\nu(\text{C-N})$	1400	1420	1426	1365	1436	1469	1475
34	$\rho(\text{NH})$	1150	1137	1150	1119	1085	1140	1182
20	$\nu(\text{C-S})$	780	748	780	723	719	733	726
Mean Absolute Deviation			77.71	80.43	78.43	105.43	79.57	82.57

^c Vibrational modes, ν -stretching, ν_{as} -asymmetric stretching, ν_s - symmetric stretching, δ - in-plane deformation, ρ -rocking.

A scatter plot of the ratios of the experimental frequencies to the calculated harmonic frequencies, $f(\text{exp})/f(\text{calc})$, against the calculated harmonic frequencies $f(\text{calc})$ with different DFT methods is shown in Fig. 3.

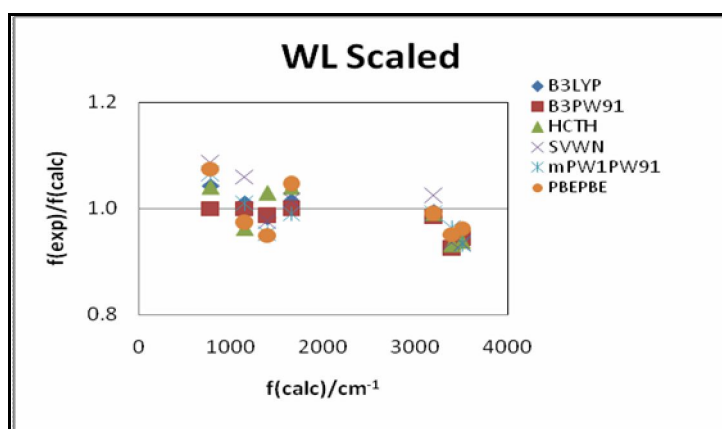


Fig. 3. Plot of the ratios of the experimental frequencies to the WLS-scaled calculated harmonic frequencies, $f(\text{exp})/f_{\text{WLS}}(\text{calc})$, against the WLS-scaled calculated harmonic frequencies with different methods for 2-propylpyridine-4-carbothioamide

The relationship between scale factors and calculated harmonic frequencies can be obtained from the Fig. 3 which are

$f(\text{exp})/f(\text{calc}) = 1.047 - 0.00003 * f(\text{calc})$	for B3LYP	(1)
$f(\text{exp})/f(\text{calc}) = 1.023 - 0.00002 * f(\text{calc})$	for B3PW91	(2)
$f(\text{exp})/f(\text{calc}) = 1.023 - 0.00002 * f(\text{calc})$	for HCTH	(3)
$f(\text{exp})/f(\text{calc}) = 1.085 - 0.00004 * f(\text{calc})$	for SVWN	(4)
$f(\text{exp})/f(\text{calc}) = 1.039 - 0.00002 * f(\text{calc})$	for mPW1PW91	(5)
$f(\text{exp})/f(\text{calc}) = 1.040 - 0.00002 * f(\text{calc})$	for PBEPBE	(6)

respectively.

The calculated IR and Raman spectra of 2-propylpyridine-4-carbothioamide with various density functional methods using Aug-CC-pVDZ basis set is shown in Fig. 4 and Fig. 5.

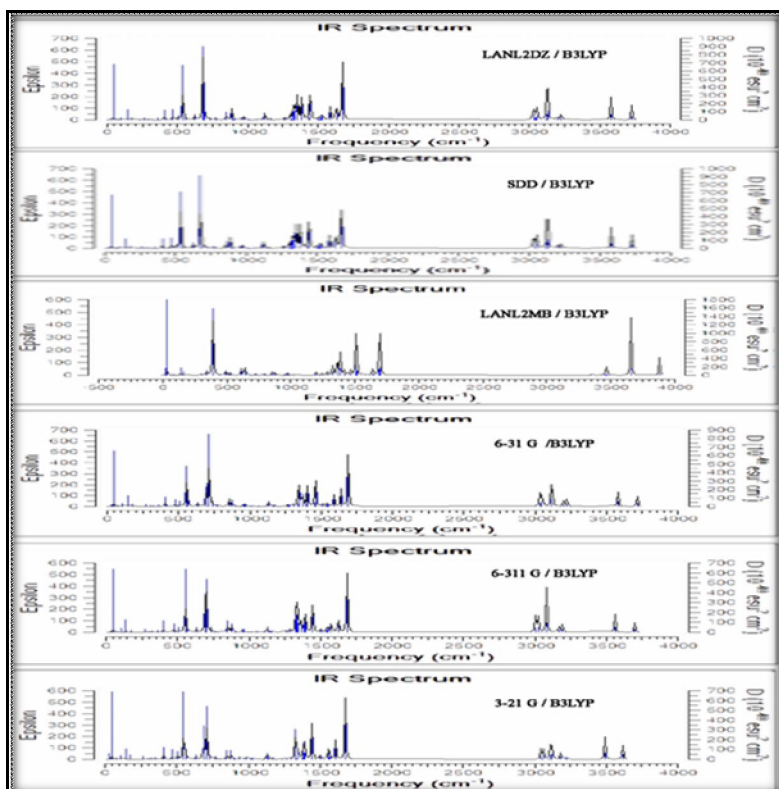


Fig. 4. The theoretical IR Spectra of 2-propylpyridine-4-carbothioamide.

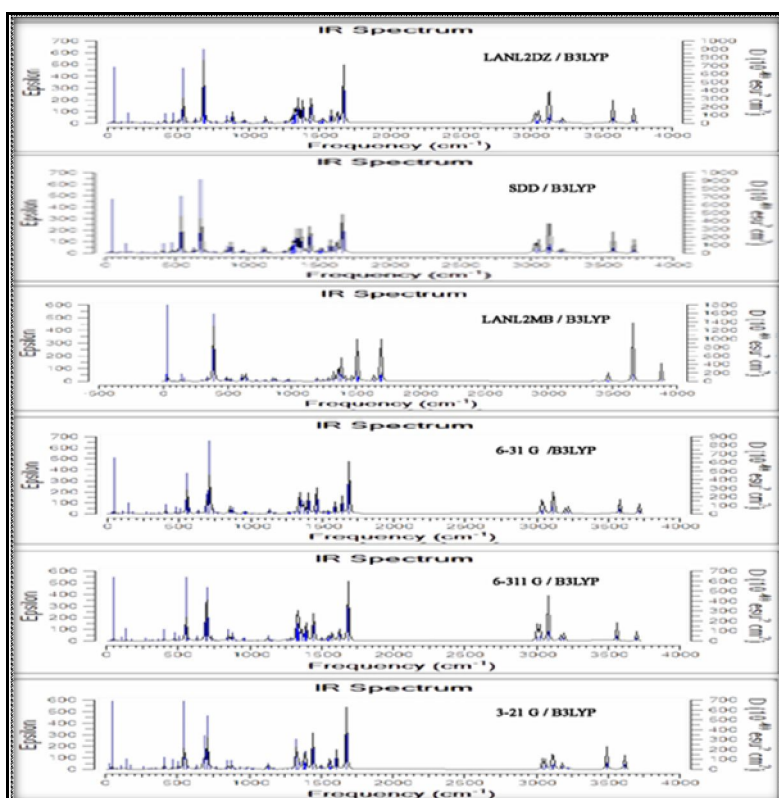


Fig. 5. The theoretical Raman Spectra of 2-propylpyridine-4-carbothioamide.

It is clear from the plot that the scaled factor of B3LYP method has better correction effect on the calculated harmonic frequencies than other methods. It is remarkable that the B3LYP method perform well for the calculation of vibrational frequencies with the mean absolute deviation significantly less than those reported

for other methods and therefore it is confirmed that B3LYP method is the best method to predict the vibrational spectra of the molecule [20-21].

3.4 Vibrational spectra calculated with the Aug-CC-pVDZ method at various basis sets

The computed vibrational frequencies (scaled) and their relative IR intensities of the molecule with B3LYP method at various basis sets is listed in Table 4.

Table 4 Scaled frequencies ^a (cm⁻¹) and infrared intensities ^b (km/mol) calculated for 2-propylpyridine-4-carbothioamide with B3LYP method using various basis sets.

Mode	Assignment	Description	LANL2DZ	SDD	LAN2MB	6-31 G	6-311 G	3-21 G
			B3LYP					
66	$\nu_{as}(\text{NH}_2)$	3500	3728	3628	3657	3650	3699	3655
65	$\nu_s(\text{NH}_2)$	3400	3581	3525	3539	3578	3560	3580
64	$\nu(\text{C-H})$	3200	3235	3269	3232	3238	3206	3263
53	$\delta(\text{ring})$	1650	1630	1629	1550	1639	1625	1610
46	$\nu(\text{C-N})$	1400	1444	1443	1450	1406	1446	1445
34	$\rho(\text{NH})$	1150	1142	1141	1190	1156	1150	1144
20	$\nu(\text{C-S})$	780	751	857	735	737	733	730
<i>Mean Absolute Deviation</i>			<i>77.86</i>	<i>67.43</i>	<i>80.43</i>	<i>61.71</i>	<i>69.00</i>	<i>77.00</i>

^c Vibrational modes, ν -stretching, ν_{as} -asymmetric stretching, ν_s - symmetric stretching, δ - in-plane deformation, ρ -rocking.

A scatter plot of the ratios of the experimental frequencies to the calculated harmonic frequencies, $f(\text{exp})/f(\text{calc})$, against the calculated harmonic frequencies $f(\text{calc})$ with different DFT methods is shown in Fig. 6.

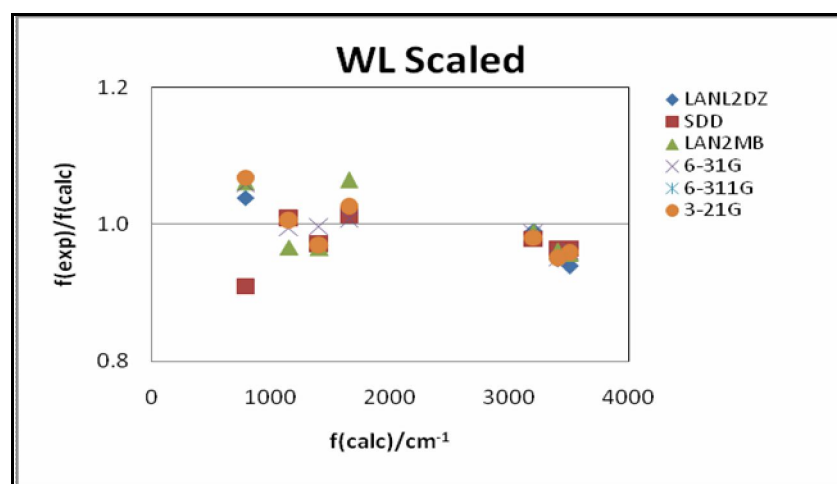


Fig. 6. Plot of the ratios of the experimental frequencies to the WLS-scaled calculated harmonic frequencies, $f(\text{exp})/f(\text{calc})$, against the WLS-scaled calculated harmonic frequencies with B3LYP method at different basis sets for 2-propylpyridine-4-carbothioamide.

The relationship between scale factors and calculated harmonic frequencies can be obtained from the Fig. 6 which are

$f(\text{exp})/f(\text{calc})=1.039-0.00002*f(\text{calc})$	<i>for LANL2DZ</i>	(1)
$f(\text{exp})/f(\text{calc})=0.968-0.000002*f(\text{calc})$	<i>for SDD</i>	(2)
$f(\text{exp})/f(\text{calc})=1.040-0.00002*f(\text{calc})$	<i>for LANL2MB</i>	(3)
$f(\text{exp})/f(\text{calc})=1.047-0.00003*f(\text{calc})$	<i>for 6-31G</i>	(4)
$f(\text{exp})/f(\text{calc})=1.045-0.00002*f(\text{calc})$	<i>for 6-311G</i>	(5) and
$f(\text{exp})/f(\text{calc})=1.053-0.00003*f(\text{calc})$	<i>for 3-21G</i>	(6)

respectively.

It is clear from the plot that the scaled factor of B3LYP/6-31 G method has better correction effect on the calculated harmonic frequencies than other methods. With the application of scaling procedure, the scaled frequencies of B3LYP agree very well with the experimental data.

4. Conclusions

In the present study, the comparative performance of different DFT methods at different basis sets in the accurate calculations of molecular structure and vibrational spectra of the title molecule has been investigated. It can be concluded from the calculation results, that B3LYP/ Aug-CC-pVDZ level affords the best quality to predict the structure of the molecule. The calculated results also indicate that the B3LYP /6-31 G level offers the highest certainty to predict the vibrational spectra of 2-propylpyridine-4-carbothioamide.

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