



A COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDIES OF 1,10-PHENANTHROLINE HYDROBROMIC ACID

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Abstract: The SEST cultured 1,10-Phenanthroline and Hydrobromic acid (PHBA) crystal testified by single crystal XRD to belong to monoclinic group. The parameters of molecular structure and vibrational frequencies of PHBA have been procured using density functional theory (DFT) technique in the B3LYP approximation and 6-31G++(d,p) basis set. Based on potential energy distribution function FT-IR, FT-Raman vibrational assignments values are calculated. Using time-dependent density functional theory (TD-DFT) cut off wavelength of PHBA in UV-Vis spectrum predicted. Using DFT method, drawn the molecular electrostatic potential map of PHBA.

Index Terms - 1,10-Phenanthroline Hydrobromic acid, XRD, FTIR, Raman Spectroscopy.

I. INTRODUCTION

1,10-Phenanthroline (phen) is a pristine chelating ligand for ions of transition element quite significant in the development of coordination chemistry [1,2,3]. Persistent being a versatile starting material for organic, inorganic and supramolecular chemistry. Recently, Computational studies of molecular and spectroscopic properties on 1,10 Phenanthroline with hydrofluoric acid and aryloxyacetic acid have been reported [4,5,6].

II. EXPERIMENTAL

The PHBA single crystal 1,10 Phenanthroline ($C_{12}H_8N_2$) and Hydrobromic acid (HBr) materials, is synthesized in the stoichiometric ratio. A measured quantity of the material is dissolved in deionized water solvent. The entire volume of the solution is stirred constantly and vigorously by magnetic stirrer for 5 hours to obtain homogeneous solution. The filtrate obtained from filtering with a quality paper is devoid of suspended impurities is then allowed to crystallize under slow evaporation. The Phen-HBr salt is obtained on evaporating the solvent. The resultant precipitate compound settled is sieved, dried at room temperature and recrystallized with water for purity. The grown component is harvested after a period of two weeks. The grown crystals are optically transparent and non-hygroscopic is depicted in Figure 1.



Figure. 1. As Grown PHBA Crystal

2.1 Computational studies

The Cartesian coordinates of the PHBA are created using ChemBio draw 11.0. The Density Functional Theory (DFT) calculations compute with a hybrid functional B3LYP/6-31++G(d,p). The Gaussian 03W package executes the data. The optimized crystal structure shown in Figure 2.

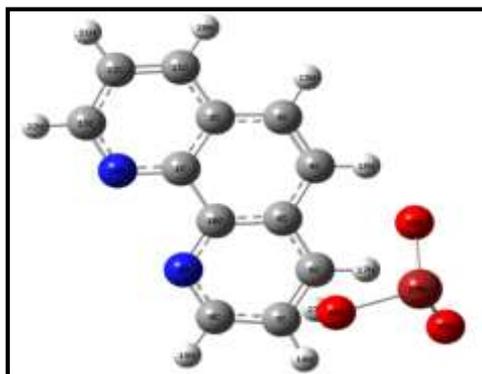


Figure. 2. Optimized Structure of PHBA

III RESULTS AND DISCUSSION

3.1. X-Ray Diffraction

The estimated cell parameters of PHBA crystal are $a=11.31\text{\AA}$, $b=6.71\text{\AA}$, $c=12.13\text{\AA}$ and interfacial angles are $\alpha=\gamma=90^\circ$, $\beta=90.51^\circ$ and Volume, $V=920\text{ (\AA)}^3$. It was found the PHBA crystal belongs to monoclinic system. $\beta=90.51^\circ$ and Volume, $V=920\text{ (\AA)}^3$

3.2. Fourier transform infrared (FTIR) and FT-Raman spectroscopic analysis

The O-H stretching band is characterized by the very broadband appearance of the broadband near about $3400\text{--}3600\text{ cm}^{-1}$ [7]. The corresponding modes occur in the experimental FTIR and FT-Raman at 3472 and 3474 cm^{-1} , respectively, for PHBA. The calculated value occurs at 3472 cm^{-1} using B3LYP/6-31++G(d,p).

The C-H stretching vibrations of aromatic and heteroaromatic structure occur in the region of $3100\text{--}2900\text{ cm}^{-1}$ [8]. A Weak band is observed at 3059 , 3081 and 3098 cm^{-1} in infrared and the intense band observed at 3065 , 3080 and 3096 cm^{-1} in FT-Raman are assigned to C-H stretching, respectively. The theoretically scaled vibrations occur at 3061 , 3080 and 3094 cm^{-1} that are found in good agreement with the experimentally recorded values.

The C-N stretching vibration is traced at 1309 and 1308 cm^{-1} in the FT-IR and FT-Raman spectrum of PHBA. The theoretically computed wavenumber at 1311 cm^{-1} in B3LYP method is correlated with the experimental observations. The C-C stretching modes are expected between the range of $1625\text{--}1430\text{ cm}^{-1}$. The actual position of these modes is determined not too much by the nature of the substituents but by the form of substitution around the ring [9]. With reference to the above literature value, the bands that appear at 1492 , 1543 , 1588 & 1611 cm^{-1} in the FT-IR and bands at 1494 , 1543 , 1584 & 1608 cm^{-1} in the FT-Raman of PHBA can be attributed to the C-C stretching vibrations respectively. The calculated bands observed in the same region show band positions at 1491 , 1543 , 1584 & 1609 cm^{-1} for the C-C stretching vibrations and match with the experimental observations of FT-IR and FT-Raman spectra. The Figure 3 and 4 show a comparative study of the Theoretical and Experimental FT-IR & FT-Raman spectrum of PHBA.

Weak band is observed at 3059 , 3081 & 3098 cm^{-1} in infrared and intense band is observed at 3065 , 3080 & 3096 cm^{-1} in FT-Raman due to the C-H stretching respectively. The vibrations gauged theoretically occurring at 3061 , 3080 & 3094 cm^{-1} go well with the experimentally recorded values. The C-N stretching vibration is noticed at 1309 and 1308 cm^{-1} in the FT-IR and FT-Raman spectrum of PHBA.

The wave number recorded at 1311 cm^{-1} in B3LYP method is correlated with the experimental observations. The C-C stretching modes are expected in the range from $1625\text{--}1430\text{ cm}^{-1}$. The actual position is much expressed by the form of substitution than by the nature of the substituents of these modes around the ring[10].

In consultation with the literature value, the bands that appear at 1492 , 1543 , 1588 & 1611 cm^{-1} in the FT-IR and bands at 1494 , 1543 , 1584 & 1608 cm^{-1} in the FT-Raman of PHBA, respectively, are impacted by the C-C stretching vibrations. The calculated bands located in the same region reveal that the band positions at 1491 , 1543 , 1584 & 1609 cm^{-1} for the C-C stretching vibrations agree well with the experimental observations of FT-IR and FT-Raman spectra.

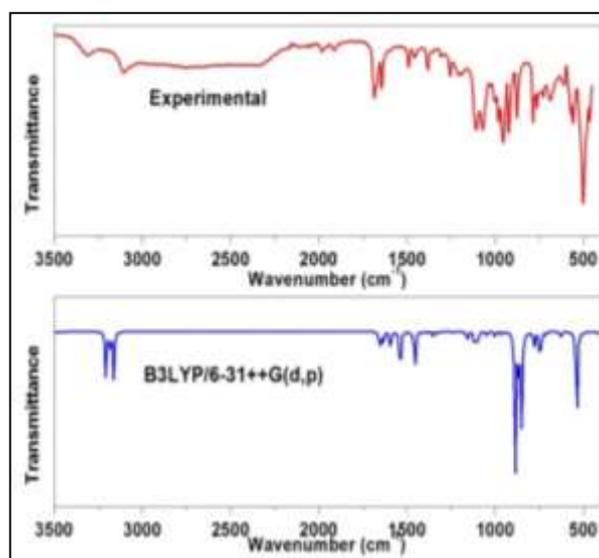


Figure. 3. FT-IR Spectrum of PHBA

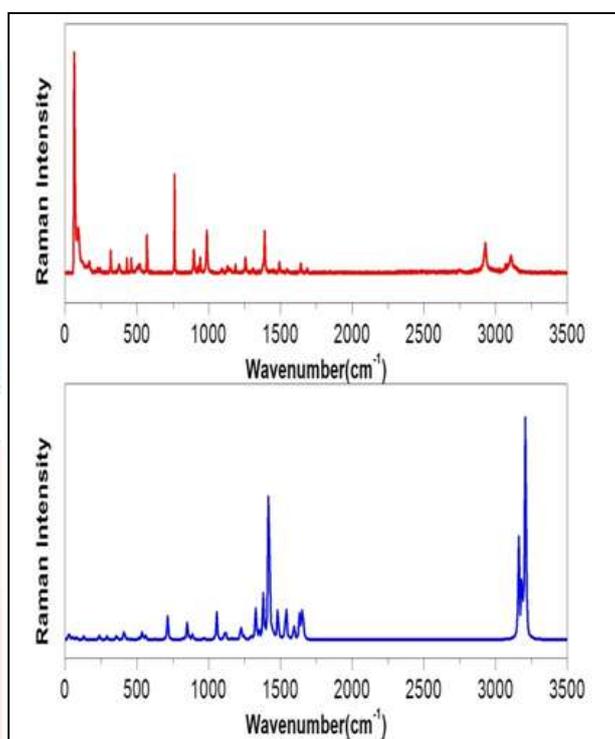


Figure. 4. FT-Raman Spectrum of PHBA

The FTIR and FT-Raman analyses confirm functional group of the studied crystal. The arrived at result is also compared with the theoretical spectrum calculated from B3LYP/6-31++G(d,p)

Table 1. Theoretical and Experimental vibrational wavenumbers (cm⁻¹) of PHBA obtained by DFT/ B3LYP method

S.No	Exp. IR	Exp. Raman	Theo Freq. Scaled	Red. Masses	Force Constant	IR Intensity	Raman Intensity	Depolar (P)	Depolar (U)
1			19	9.2507	0.0022	0.4417	231186.18	0.7493	0.8567
2			22	8.922	0.0027	0.5183	393458.18	0.7215	0.8382
3			31	8.1718	0.0049	1.101	286649.78	0.7419	0.8519
4			48	12.8775	0.0188	2.3183	25317.29	0.5152	0.68
5			53	9.1095	0.016	1.8145	79406.07	0.7455	0.8542
6		80	77	7.7303	0.029	10.5013	35272.25	0.6992	0.823
7			101	4.8625	0.0312	1.5367	828.98	0.7438	0.8531
8		123	125	5.1075	0.0501	3.1146	14923.83	0.7012	0.8244
9		226	228	3.5282	0.1154	2.6522	1191.15	0.6356	0.7772
10		230	230	3.5712	0.1186	2.2729	2009.70	0.7354	0.8475
11			233	5.2068	0.1775	3.3418	2396.30	0.6444	0.7838
12		237	236	4.8835	0.1711	0.1332	1450.08	0.7418	0.8517
13		284	284	9.0096	0.4575	14.7382	3276.25	0.7205	0.8375
14		343	345	14.5103	1.0825	26.9296	1434.04	0.6356	0.7772
15		353	351	1.3833	0.1068	48.8541	1064.69	0.2441	0.3924
16		396	398	4.1647	0.4144	0.6423	1181.16	0.371	0.5413
17		401	400	6.1403	0.6163	1.2646	3839.55	0.2334	0.3785
18		431	431	4.154	0.4851	0.0611	142.07	0.7457	0.8543
19	464	455	450	6.2922	0.8021	0.3815	340.41	0.7486	0.8562
20	481	482	481	3.3478	0.4859	1.0576	77.69	0.7305	0.8443
21	502	501	503	4.9759	0.7898	0.7573	477.36	0.7498	0.857
22	521	519	521	15.4942	2.6404	93.4663	2500.34	0.2036	0.3383
23			541	4.6006	0.8472	0.1095	551.58	0.2169	0.3564
24	548	542	542	4.6428	0.8584	0.2827	486.32	0.1857	0.3132
25	589	596	591	3.635	0.7987	0.0307	64.53	0.3165	0.4808
26	608	607	609	8.0312	1.87	6.7452	142.17	0.7342	0.8467
27	692	696	691	6.8795	2.0643	2.8814	3477.28	0.051	0.097
28	717	719	715	6.2104	1.9926	3.23	18.68	0.5703	0.7264
29	727	725	723	3.8005	1.249	32.2574	13.74	0.6541	0.7909
30	751	762	756	1.2289	0.4411	16.204	6.75	0.4182	0.5898
31	804	795	797	1.3037	0.5208	0.5808	111.41	0.6403	0.7807
32		820	821	2.5647	1.0855	34.4531	312.01	0.0772	0.1433
33			823	8.9513	3.8095	50.8818	1349.56	0.0627	0.1179
34	837	837	838	2.9888	1.3172	37.1243	13.43	0.7066	0.8281
35			841	6.2318	2.7677	5.3458	172.46	0.1423	0.2492
36		855	858	17.7572	8.2049	114.9618	384.92	0.6677	0.8007
37	866	864	866	5.1832	2.4442	5.7908	97.63	0.75	0.8571
38	928	931	934	1.3308	0.7298	0.0349	75.55	0.7422	0.852
39			936	1.3833	0.7606	2.0185	18.46	0.1761	0.2995
40	942	942	946	1.3619	0.7662	0.4662	54.83	0.7083	0.8292
41	963	969	968	1.3638	0.8022	0.7676	1.74	0.6648	0.7987
42	980	982	973	1.2966	0.7714	4.1358	11.62	0.6637	0.7978
43		1011	1015	4.8147	3.1166	3.0999	92.53	0.6842	0.8125
44	1026	1028	1024	2.5595	1.6857	0.6968	1586.99	0.0557	0.1055
45	1050	1052	1058	2.4947	1.7536	2.8616	3.06	0.1677	0.2872
46	1070	1073	1069	1.1569	0.8302	8.053	35.51	0.324	0.4895
47		1089	1081	2.0325	1.4912	16.827	708.94	0.0527	0.1001

48		1122	1123	1.2291	0.9735	9.7337	56.84	0.7059	0.8276
49		1133	1132	1.2471	1.0042	0.7926	61.09	0.5603	0.7182
50	1185	1188	1186	2.1416	1.8918	0.6493	861.58	0.1785	0.303
51		1198	1195	2.1119	1.8935	0.0689	72.32	0.4179	0.5894
52	1207	1205	1208	1.8011	1.6505	0.7939	143.07	0.7338	0.8465
53	1255	1256	1255	1.8762	1.8569	1.0543	153.78	0.7432	0.8527
54		1285	1287	3.4245	3.5652	2.2822	1456.29	0.2943	0.4547
55	1309	1308	1311	6.7951	7.3339	4.1049	232.80	0.7324	0.8455
56	1342	1342	1339	2.1655	2.4385	1.402	1654.78	0.2185	0.3586
57	1373	1379	1375	4.0093	4.7645	1.7485	7366.08	0.2453	0.3939
58	1401		1402	1.7536	2.1643	0.0127	186.16	0.7353	0.8474
59		1408	1410	2.2711	2.8365	41.5787	77.63	0.7312	0.8447
60	1438	1438	1436	2.8047	3.6316	1.1245	1086.49	0.1846	0.3116
61			1485	3.3282	4.6116	11.1257	74.53	0.5672	0.7238
62	1492	1494	1491	4.0492	5.6547	34.3748	1315.85	0.1569	0.2713
63	1543	1543	1543	6.4711	9.6824	19.511	517.38	0.7257	0.8411
64	1588	1584	1584	5.7898	9.1223	10.2797	748.43	0.4935	0.6608
65			1598	6.3677	10.2143	10.8172	610.95	0.7495	0.8568
66	1611	1608	1609	6.3119	10.2726	5.9885	397.86	0.0738	0.1374
67	3059	3065	3061	1.0893	6.4114	23.1216	293.26	0.4582	0.6284
68			3062	1.0895	6.418	23.1251	311.44	0.3085	0.4716
69	3081	3080	3080	1.0887	6.4878	0.0703	8.87	0.1465	0.2556
70			3083	1.0887	6.499	14.5125	303.44	0.6087	0.7568
71	3098	3096	3094	1.0888	6.548	2.7456	141.90	0.6404	0.7808
72			3104	1.0955	6.6327	10.2876	166.42	0.4191	0.5907

3.1. UV-Vis Spectrum analysis

The calculated absorption maxima values have been inferred to be 24920nm for gas phase from Gaussian 03 W at DFT/B3LYP/6-31G (d,p) method and the experimental results are observed at 250.32 nm. The Experimental and theoretical UV-vis spectrum of PHBA displayed in Figure 3.

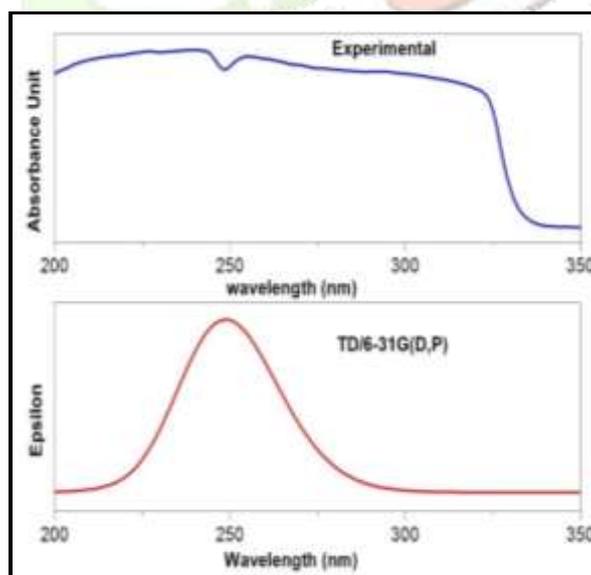


Figure 5 UV-Vis Spectrum of PHBA

3.2 Molecular Electrostatic Potential (MEP)

MEP is used mainly for predicting sites and relative reactivities towards electrophilic hit, in studies of biological identification and hydrogen bonding contacts [11]. To calculate the reactive sites of electrophilic and nucleophilic attack for PHBA, the MEP at the B3LYP/6-31++G(d,p) method is applied as shown in Figure 5. The values of the electrostatic potential at the surface are represented in different colors. The diagram shows that nitrogen atom represents the most negative potential region (dark red).

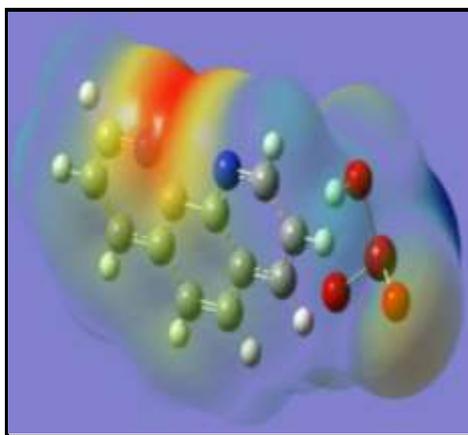


Figure 6. MEP of PHBA

IV. CONCLUSION

The physico chemical properties of PHBA organic crystal was analyzed. And investigated the vibrational spectra of FT-IR, FT-Raman of PHBA. Cut off wavelength of PHBA was calculated by TD-DFT method and compared with experimental UV-Vis spectra. MEP plays a vital role in finding the electrophilic and nucleophilic attack of the PHBA molecule.

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