DENSITY FUNCTIONAL THEORY CALCULATIONS AND VIBRATIONAL ANALYSIS OF 6–NITROVERATRALDEHYDE AND NITRO SUBSTITUTIONAL EFFECT OF VERATRALDEHYDE

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Abstract

Complete vibrational analysis of FT–IR and FT–Raman spectra of 6–nitroveratraldehyde is carried out. Its minimum energy is calculated. The molecular geometry, vibrational frequencies, Force constants IR intensities and Raman activities of 6–nitroveratraldehyde have been calculated using the Density Functional Theory. A detailed assignment of all the fundamental modes has been done using potential energy distribution. Molecular geometries for nitroveratraldehyde (VA) and 6–nitroveratraldehyde(6NVA) have been calculated and compared along with the HOMO LUMO analysis in order to indentify the substitutional effect of nitro group in the 6^{th} place of veratraldehyde. It is observed that the internal bond angles at the carbon atoms to which the nitro group is attached in veratraldehyde (C5–C6–C1) does not show any marked deviation from the normally adopted internal bond angles from 119.9996^0. But, the external bond angles at the hydrogen atom is replaced by the nitro group (H12–C6–C1 and N12–C5–C6) have the marked deviation from 120.0002^0 to 123.22^0 due to the nitro group substitution in the 6^{th} places of the benzene ring.

Keywords: DFT, FTIR, HOMO, LUMO.

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1. Introduction

Veratraldehyde (3,4–dimethoxybenzaldehyde) is an organic compound that is widely used as a flavorant and odorant. The compound is structurally related to benzaldehyde. This compound is popular commercially because of its pleasant woody fragrance. It is derivative of vanillin, from which it is prepared by methylation. Veratraldehyde can be used as an intermediate in the synthesis of some pharmaceutical drugs including amiquinsin, hoquizil, piquizil, prazosin, quinazocin, tiapamil, toborinone, verazide, and vetrabutine [1]. On considering the above applications, the 6–nitroveratraldehyde (6NVA) in which nitro group was substituted in the sixth place of the veratraldehyde (VA) was taken into consideration for the spectral investigation and DFT calculations in this work.

2. Experimental details

Fourier Transforms Infrared spectral measurements of 6–nitroveratraldehyde were performed in the region 4000–400 cm^{-1} at room temperature using FTIR spectrometer (Tensor 37). FT–Raman spectra were acquired at room temperature in the range of 4000–50 cm^{-1} at 2 cm^{-1} spectral resolution on Bruker RFS–27 spectrometer using 1064 nm line of Nd:YAG laser as excitation source and laser power was set at 100 mW.

3. Computational details

Density Functional Theory calculations are performed using GAUSSIAN program package[2] and the visual inspection was carried out using GAUSSVIEW program [2]. The structure was optimized by assuming C1 point group of symmetry. The definition of internal co–ordinates and the assignment of the fundamental modes based on potential energy distribution (PED) was carried out.

4. Results and Discussion

4.1. Molecular geometry

The optimized molecular geometries of nitroveratraldehyde and 6–nitroveratraldehyde along with numbering of atoms are as shown in figures 1 and 2 respectively. The global minimum energy obtained for nitroveratraldehyde for the structure optimization was found to be –2.692654D–07a.u. and the global minimum energy obtained for 6–nitroveratraldehyde structure optimization was found to be –9.338893D–08a.u. The comparative optimized geometrical parameters for nitroveratraldehyde and 6–nitroveratraldehyde (bond length and bond angles) were listed in table 1.

From the values it was observed, that the internal bond angles at the carbon atoms to which the nitro group is attached in veratraldehyde (C5–C6–C1) does not show any marked deviation from the normally adopted internal bond angles from 119.9996^0. But, the external bond angles at the hydrogen atom is replaced by the nitro group (H12–C6–C1 and N12–C5–C6) have the marked deviation from 120.0002^0 to 123.22^0 due to the nitro group substitution in the 6^{th} places of the benzene ring This shows that the substituent groups are influencing the optimized geometry of the compound.

HOMO LUMO analysis were done and from that the energy gaps were determined and which was 0.16513 for veratraldehyde and 0.14956 for 6–nitroveratraldehyde. the energy gap was decreased due to the substitutional effect of nitro group in the veratraldehyde molecule. It is shown in the figures 3 and 4.

Experimental FT–IR and FT–Raman spectrums were taken for the 6–nitroveratraldehyde and the calculated spectrums of FT–IR and FT–Raman were drawn using GAUSSVIEW program. The comparision of experimental and theoretical FT–IR and FT–Raman spectrum are shown in figures 5 and 6. DFT calculations were done using Gaussian 2003 software[2] using the basis set B3LYP/6–31G*, from that the calculated reduced mass, force constant, IR intensity, Raman activity are listed in the table 2.

Table 1: Molecular Geometry (Bond length and Bond angles of 6NVA and VA)

Parameters	Bond length (Å)		Parameters	Bond angle (°)	
	veratr-aldehydel	6–nitrover-atraldehydel		veratr-aldehydel	6–nitrover-atraldehydel
C(1)–H(7)	1.1	1.1	H(14)–C(13)–H(15)	109.52	109.52
C(2)–C(1)	1.3948	1.3948	H(14)–C(13)–H(16)	109.4618	109.4618
C(1)–C(6)	1.3949	1.3949	H(14)–C(13)–O(8)	109.4618	109.4618
C(13)–H(15)	1.113	1.113	H(15)–C(13)–H(16)	109.4418	109.4418
C(13)–H(16)	1.113	1.113	H(15)–C(13)–O(8)	109.4418	109.4418
C(17)–H(20)	1.113	1.113	H(16)–C(13)–O(8)	109.5	109.5
C(17)–H(19)	1.113	1.113	C(13)–O(8)–C(2)	120	120
C(17)–H(18)	1.113	1.113	H(20)–C(17)–H(19)	109.52	109.52
C(4)–H(10)	1.1	1.1	H(20)–C(17)–H(18)	109.4618	109.4618
C(11)–H(21)	1.113	1.113	H(20)–C(17)–O(9)	109.4618	109.4418
C(11)–O(22)	1.208	1.208	H(19)–C(17)–H(18)	109.4418	109.4418
C(5)–C(6)	1.3948	1.3948	H(19)–C(17)–O(9)	109.4418	109.4618
C(13)–H(14)	1.113	1.113	H(18)–C(17)–O(9)	109.5	109.5
C(6)–H(12)	1.1	–-	H(21)–C(11)–O(22)	120	120
O(8)–C(13)	1.402	1.402	H(21)–C(11)–C(5)	120	120
C(2)–O(8)	1.355	1.355	O(22)–C(11)–C(5)	120	120
C(3)–C(2)	1.3948	1.3948	C(1)–C(2)–O(8)	119.9991	119.9991
O(9)–C(17)	1.402	1.402	C(1)–C(2)–C(3)	120.0018	120.0018
C(3)–O(9)	1.355	1.355	O(8)–C(2)–C(3)	119.9991	119.9991
C(4)–C(3)	1.3949	1.3949	C(17)–O(9)–C(3)	120	120
C(5)–C(4)	1.3948	1.3948			
C(11)–C(5)	1.351	1.351			
C(6)–N(12)	—	1.248			
N(12)–O(24)	—	1.31			
N(12)–O(23)	—	1.31			

4.2. Molecular vibrations and stimulated spectra

The compounds, veratraldehydes and 6–nitroveratraldehyde both belongs to C1 point group symmetry and consist of 22 atoms and 24 atoms respectively. Veratraldehyde possesses 60 fundamental modes of vibrations and they are distributed among the symmetry species as: Γvib = 41 (in–plane) + 19 (out–of–plane) and 6–nitroveratraldehyde possesses 66 fundamental modes of vibrations and they are distributed among the symmetry species as: Γvib = 45 (in–plane) + 21 (out–of–plane). All vibrations are active in both the Raman scattering and infrared absorption.

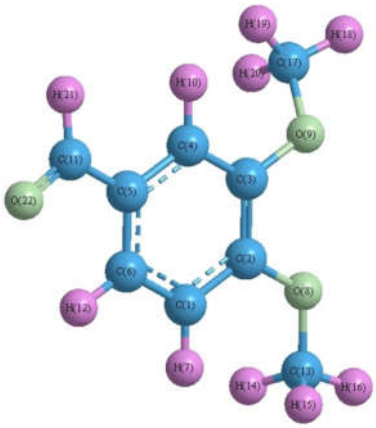


Figure 1: Molecular structure of veratraldehydel

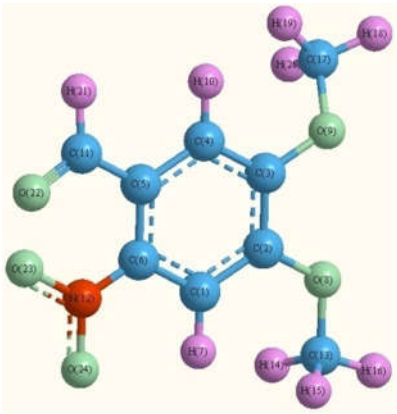
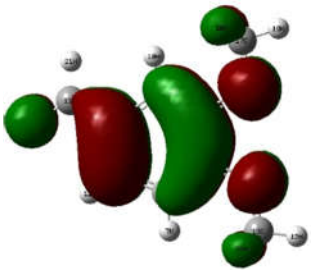
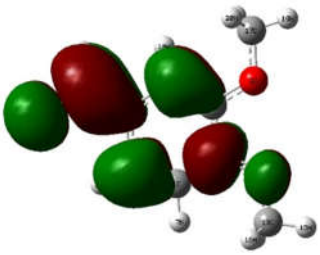


Figure 2: Molecular structure of 6–nitroveratraldehydel



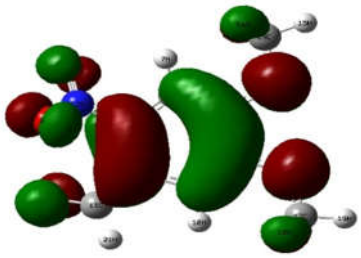
HOMO = – 0.04942



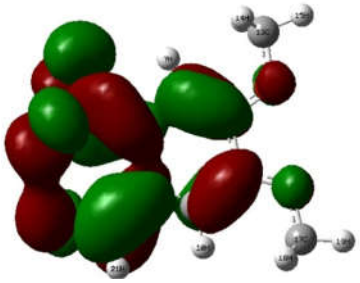
LUMO = – 0.21455

Energy gap = 0.16513

Figure 3: HOMO-LUMO of veratraldehydel



HOMO = – 0.08639



LUMO = – 0.23595

Energy gap = 0.14956

Figure 4: HOMO-LUMO of 6–nitroveratraldehydel

4.3. Vibrational analysis and assignment

The well known good performance of density functional theory for the estimation of vibrational spectra of organic compounds is well observed in the case of the title compound.

C–H Vibrations

Aromatic compounds commonly exhibit multiple weak band in the region 3100–3000 cm^{-1} due to aromatic C–H stretching vibrations. In the present study the bands appears at 2970 cm^{-1} in IR spectrum and 3103 cm^{-1} and 3030 cm^{-1} in Raman spectrum are assigned to C–H stretching vibrations. The C–H out–of–plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm^{-1}. Hence, the bands appeared at 803 cm^{-1}, 778 cm^{-1}, 720 cm^{-1}, 654 cm^{-1} in IR spectrum and 808 cm^{-1}, 706 cm^{-1} in Raman spectrum of the title compound have been assigned to C–H out–of–plane bending vibrations. They are in good agreement with the literature values [3–5].

C–C vibrations

Benzene has two degenerate modes, e2g (1596 cm^{-1}) and e1u (1485 cm^{-1}), and two non–generate modes, b2u (1310 cm^{-1}) and a1g (995 cm^{-1}), due to skeleton stretching of C–C bonds. Bands between 1300 cm^{-1} and 1650 cm^{-1} are assigned to C–C stretching modes. In the IR spectrum, the bands at 1521 cm^{-1}, 1420 cm^{-1} and 1416 cm^{-1} are assigned to C–C stretching vibrations. In the Raman Spectrum, the bands at 1605 cm^{-1}, 1522 cm^{-1} and 1488 cm^{-1} are assigned to C–C stretching vibrations. In all these modes, the contribution of C–C stretching vibrations are present along with the rings' deformation.

C=O Vibrations

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. Normally this multiply bonded group is highly polar and therefore gives rise to an intense infrared absorption band. The position of the C=O stretching vibration is very sensitive to various factors, such as the physical state, electronic effects by substituent, ring strains, etc. [6]. Consideration of these factors provides further information about the environment of the C=O group. The carbonyl stretching generally occurs as a strong absorption in the region from 1730 to 1645 cm^{-1}. This portion of the infrared and Raman spectrum is most useful because the position of the carbonyl absorption is quite sensitive to substitution effects and the geometry of the molecule. In the present investigation, the peak identified at 1650 cm^{-1} in IR spectrum have been assigned to C=O stretching vibrations.

C–N Vibrations

Since the mixing of vibrations is possible, identification of C–N vibrations is a difficult task. However, with the help of force field calculations C–N vibrations are identified and assigned. The unconjucated C–N linkage in the nitro give medium to weak bands near 1250–1020 cm^{-1} because of C–N stretching vibrations. The medium peak in IR spectrum at 1020 cm^{-1} and a medium peak in Raman spectrum at 1220 cm^{-1} are assigned to C–N stretching vibr, ations [7].

Ring vibrations

Ring modes are affected due to substitution in the aromatic ring [8] and in–plane deformation vibration is at higher frequencies than the out–of–plane vibration [9]. In the present work, the frequencies observed at 1650, 1562 cm^{-1} in IR spectrum and 1605 cm^{-1} in Raman spectrum are assigned to C–C stretching vibrations. The in–plane vibration is observed at 1020 cm^{-1} and the out–of –plane vibration is observed at 970 cm^{-1}. The theoretical computed values are well agreed with the experimental data.

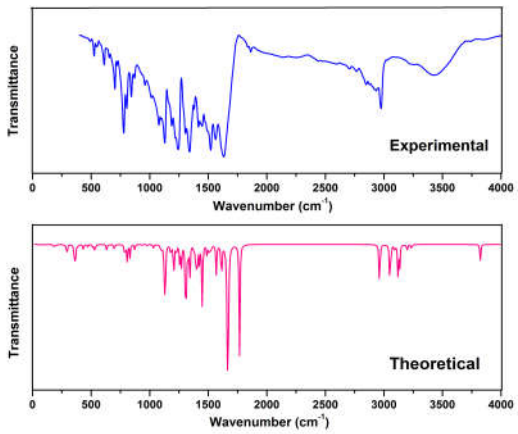


Figure 5: Experimental and Theoretical FT–IR spectra of 6NVA

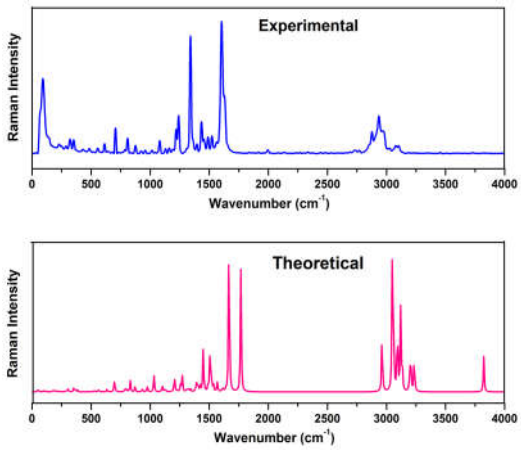


Figure 6: Experimental and Theoretical FT– Raman spectra 6NVA

Table 2: Calculated frequencies and vibrational assignments of 6NVA based on B3LYP/6–31G* Calculations

Mode No.	Observed Frequencies		Calculated Frequencie (Scaled)	Reduced mass	Force constant	IR Intensity	Raman Activity	Assignments
	IR	Raman						
1.	–	40	42	7.8055	0.0085	0.2407	0.9221	C–O–C–C (torsional)
2.	–	63	65	6.0077	0.0151	0.1968	1.1195	C–O–C–C (torsional)
3.	–	85	80	3.7126	0.0140	2.7855	0.4525	O–O–C–C (torsional)
4.	–	112	109	4.5166	0.0318	10.0160	3.3593	O–C–C (bending)
5.	–	130	135	4.9628	0.0535	4.0058	0.9912	C–C–C–C (torsional)
6.	–	159	157	4.3076	0.0626	1.7084	0.6249	O–C–C–C (torsional)
7.	–	170	172	3.5516	0.0620	4.5886	2.0055	C–C–C (bending)
8.	–	179	181	3.9212	0.0764	2.9347	2.1129	O–C–O–N (wagging)
9.	–	190	200	8.1117	0.1924	1.6938	1.0207	C–O–C (bending)
10.	–	230	229	1.4115	0.0439	2.3253	1.3189	C–O–C (bending)
11.	–	245	242	1.2022	0.0416	0.1009	0.8099	C–C–C (bending)
12.	–	286	287	2.0418	0.0996	1.9482	1.4953	C–C–C – C (torsional)
13.	–	295	296	5.2302	0.2715	0.9098	1.7168	C–C–C–C (wagging)
14.	–	316	318	6.2533	0.3742	3.1281	1.6610	N–C–C–C (wagging)
15.	–	–	358	4.9458	0.3752	1.4405	12.171	O–C–C–C (wagging)
16.	–	–	375	5.4502	0.4518	2.2316	1.8128	O–C–C–C (wagging)
17.	–	440	443	5.5425	0.6432	5.9441	4.1028	O–C–C (bending)
18.	–	–	477	3.8020	0.5104	0.3045	0.9972	C–C–C (bending)
19.	–	500	498	6.4572	0.9456	2.7727	1.6761	O–O (stretching)
20.	530	–	535	6.6873	1.1295	10.6612	0.7261	O–C–C (bending)
21.	614	610	611	6.0576	1.3352	11.8452	1.8739	C–C–C–C (torsional)
22.	–	665	668	6.0425	1.5901	6.3371	2.5670	H–C–C–C (torsional)
23.	–	685	681	8.2602	2.2612	11.6526	4.2682	H–C–C–C (torsional)
24.	720	–	709	5.0087	1.4857	3.6858	0.4939	H–C–O–O (torsional)
25.	760	–	751	7.0947	2.3590	11.3771	1.7942	O–O–C (bending)
26.	794	795	799	6.1049	2.2966	68.6343	22.043	N–C–C (bending)
27.	–	820	822	6.4114	2.5572	28.9750	2.2469	O–N–O (bending)

28.	–	861	864	1.4448	0.6365	5.4254	3.8463	O–C (stretching)
29.	878	872	874	3.9165	1.7661	7.6520	2.5251	O–C (stretching)
30.	–	882	885	1.5575	0.7198	31.5805	1.4357	O–C (stretching)
31.	–	–	1009	2.0323	1.2202	0.2795	5.3086	O–C (stretching)
32.	1023	–	1022	4.9465	3.0492	5.4618	2.2725	C–C (stretching)
33.	1062	1062	1075	6.4179	4.3737	11.2939	1.4404	O–C (stretching)
34.	–	1110	1101	5.6633	4.0453	186.636	22.065	H–C–C (bending)
35.	1163	–	1182	1.2692	1.0460	0.7609	5.0475	H–C–C (bending)
36.	1190	1191	1184	1.2688	1.0487	0.9963	4.0485	H–C–O (bending)
37.	–	–	1206	1.8989	1.6283	103.512	11.264	C–C–C (bending)
38.	–	–	1221	1.3458	1.1825	6.7926	2.0072	C–C (stretching)
39.	1226	1227	1223	1.5268	1.3474	13.8847	19.449	C–C (stretching)
40.	1260	1260	1275	4.6083	4.4170	157.793	3.8436	C–C–C (bending)
41.	1290	1292	1299	1.5921	1.5844	38.2803	8.6892	H–C–O–C (torsional)
42.	1336	1332	1332	4.3657	4.5695	354.698	23.264	H–C–O–C (torsional)
43.	1399	1399	1390	4.4488	5.0684	138.869	23.940	H–C–H (bending)
44.	–	–	1407	13.312	15.536	299.880	184.37	H–C–H (bending)
45.	1440	–	1425	4.4644	5.3435	18.1432	9.8312	H–C–H (bending)
46.	1460	1444	1458	1.4011	1.7563	4.9063	4.3328	H–C–O–C (torsional)
47.	–	–	1500	1.2307	1.6321	22.9784	14.352	H–C–O–C (torsional)
48.	–	–	1506	1.3075	1.7483	1.3018	3.1953	H–C–H (bending)
49.	1521	–	1522	1.0469	1.4301	4.7304	26.990	H–C–H (bending)
50.	–	1523	1523	1.0473	1.4315	10.9352	25.861	H–C–H (bending)
51.	–	–	1530	1.0559	1.4563	42.3733	15.709	H–C–O–C (torsional)
52.	–	–	1531	1.0607	1.4666	44.8369	10.830	H–C–O–C (torsional)
53.	1574	1573	1573	3.2535	4.7464	142.793	7.1165	C–C (stretching)
54.	1610	1614	1620	9.2173	14.267	111.832	56.832	C–C (stretching)
55.	–	–	1642	6.8379	10.862	291.137	144.51	C–C (stretching)
56.	1665	–	1656	10.031	16.209	87.5075	86.264	N–C (stretching)
57.	–	1810	1814	10.395	20.170	224.407	106.71	O–N (stretching)
58.	2910	–	2902	1.0833	5.3774	133.098	132.32	C–H (stretching)
59.	–	3022	3033	1.0345	5.6108	56.0638	96.705	C–H (stretching)
60.	3045	–	3039	1.0341	5.6280	39.3004	133.33	C–H (stretching)
61.	3099	3091	3097	1.1072	6.2574	34.0247	52.675	C–H (stretching)
62.	–	3103	3104	1.1075	6.2907	30.9883	48.503	C–H (stretching)
63.	–	3169	3171	1.1003	6.5184	17.2574	124.79	C–H (stretching)
64.	–	3172	3173	1.1010	6.5334	18.3191	133.24	C–H (stretching)
65.	–	–	3217	1.0887	6.6386	5.5424	58.099	C–H (stretching)
66.	–	3259	3260	1.0901	6.8286	2.1206	56.444	C–H (stretching)

5. Conclusion

In this work FT–IR and FT–Raman spectra of 6–nitroveratraldehyde is analysed to carry the complete vibrational analysis. Its minimum energy is calculated. The molecular geometry, vibrational frequencies, Force constants IR intensities and Raman activities of 6–nitroveratraldehyde have been calculated using the Density Functional Theory B3LYP/6–31G* methodology. The stimulated spectra obtained from the values of the calculated frequencies were used to compare with the experimental FT–IR and FT–Raman spectra. The observed frequencies were found good agreement with the calculated frequencies. A detailed assignment of all the fundamental modes has been done using potential energy distribution. Molecular geometries for nitroveratraldehyde and 6–nitroveratraldehyde have been calculated and compared along with the HOMO LUMO analysis in order to indentify the substitutional effect of nitro group in the 6^{th} place of veratraldehyde.

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