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# Molecular Structure, Vibrational Spectral Studies and NLO Properties of 4-Benzyloxy-3-MethoxyBenzaldehyde by DFT 

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#### Abstract

Benzaldehydes and its derivatives are the simplest in aromatic aldehydes and have wide range of use in different industries, they also exhibits different biological activities. Due to this reason there exist a vast field of study of substituted benzaldehydes. In the present study 4-benzyloxy3-methoxy-benzaldehyde is taken for study. The spectral studies were performed for FTIR, IR (KBr and Nuzol) and Raman. Quantum mechanical calculations of geometries, energies, vibrational wave numbers and thermodynamic constants have been performed with Gaussian 09W program package using the Becke-3Lee-YangParr (B3LYP) functional supplemented with the standard 6-31G (DP). The optimised geometrical parameters obtained by computational method used shows good agreement with the experimental data. The thermodynamic properties as heat capacity, entropy, enthalpy and Gibb's free energy of the titled compounds at different temperatures were also calculated along with dipole moment, polarisability and hyperpolarisability.


Keywords: 4-benzyloxy3-methoxy-benzaldehyde, vibrational, NLO, Gaussian 09W, DFT/ B3LYP ,thermodynamic parameters, FTIR, dipole moment, polarisability, hyperpolarisability.

## I. INTRODUCTION

Spectroscopic studies of the benzaldehyde and their derivatives have been carried out as the vibrational spectra are very useful for understanding of specific biological activities and for the analysis of relatively complex system. Benzaldehydes have a large usage in different industries as perfumes, flavouring compounds, soaps, foods, preparations of some aniline dyes, solvent for oils etc.[1]. They have also shown anti tumour activity in mice [1,2]. In this light lots of aspects of substituted benzaldehydes and its derivatives are unexplored in spite of the fact that much work has been done on these compounds.[3-6].

## II. EXPERIMENTAL

Spec-pure grade sample of 4-benzyloxy-3-methoxy- benzaldehyde (abbreviated and further mentioned as BMB) was obtained from M/S Aldrich Chemie, West Germany. The Purity of sample was confirmed by elemental analysis and melting point determination. The laser Raman spectra of both the molecules were recorded on Spex Rama Lab spectrophotometer using 52 MW Argon-Krypton laser beam of wavelength 488 nm . The infrared spectra of these two compounds were recorded on Perkin Elmer spectrophotometer model -52 in the region $400-4000 \mathrm{~cm}^{-1}$ using KBr and nuzol technique.

## III. COMPUTATIONAL

All the calculations were carried out for BMB with Gaussian 03W program package [7]using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard $6-31 \mathrm{G}(\mathrm{DP})$ basis set further referred as DFT calculations. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the absence of imaginary values in the wave number calculations.

## IV. RESULTS AND DISCUSSION

## A. Molecular Structure

The molecular structure of the mentioned compound BMB is shown in Figure 1. The optimized bond lengths, bond angles and dihedral angles of the compound is calculated by B3LYP method using B3LYP $6-311++\mathrm{G}(\mathrm{d})$ and $6-311++\mathrm{G}(\mathrm{D}, \mathrm{P})$ basis sets are listed in Table 1 is in accordance with atom numbering scheme as shown in Fig. 1. Since the exact crystal structure of the compound BMB is not available till now, the optimized structure can only be compared with other similar system for which the crystal structures have been solved. [8]

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Figure 1
Calculated Optimized Geometrical Parameters of BMB, at B3LYP/6-31G( $\mathrm{d}, \mathrm{p}$ ): bond length ( $(\AA)$, bond angle( ${ }^{\circ}$ ), dihedral angles $\left({ }^{\circ}\right)$

| S. No | Atoms of <br> molecule | Bond length (A) | Angle between <br> atoms $\left({ }^{\circ}\right)$ | Bond angle ( ${ }^{\circ}$ ) | Dihedral angle <br> between atoms <br> $\left({ }^{\circ}\right)$ | Dihedral <br> angle ( $\left.{ }^{\circ}\right)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 1. | $\mathrm{R}(1,2)$ | 1.3952 | $\mathrm{~A}(2,1,6)$ | 119.9985 | $\mathrm{D}(6,1,2,3)$ | 0.0323 |
| 2. | $\mathrm{R}(1,6)$ | 1.3948 | $\mathrm{~A}(2,1,10)$ | 119.9972 | $\mathrm{D}(6,1,2,7)$ | 179.9532 |
| 3. | $\mathrm{R}(1,10)$ | 1.54 | $\mathrm{~A}(6,1,10)$ | 120.0043 | $\mathrm{D}(10,1,2,3)$ | -179.9729 |
| 4. | $\mathrm{R}(2,3)$ | 1.3947 | $\mathrm{~A}(1,2,3)$ | 120.0086 | $\mathrm{D}(10,1,2,7)$ | -0.052 |
| 5. | $\mathrm{R}(2,7)$ | 1.0997 | $\mathrm{~A}(1,2,7)$ | 119.9808 | $\mathrm{D}(2,1,6,5)$ | 0.0149 |
| 6. | $\mathrm{R}(3,4)$ | 1.3954 | $\mathrm{~A}(3,2,7)$ | 120.0106 | $\mathrm{D}(2,1,6,9)$ | 179.9892 |
| 7. | $\mathrm{R}(3,28)$ | 1.43 | $\mathrm{~A}(2,3,4)$ | 119.9942 | $\mathrm{D}(10,1,6,5)$ | -179.9798 |
| 8. | $\mathrm{R}(4,5)$ | 1.3948 | $\mathrm{~A}(2,3,28)$ | 120.0128 | $\mathrm{D}(10,1,6,9)$ | -0.0056 |
| 9. | $\mathrm{R}(4,13)$ | 1.43 | $\mathrm{~A}(4,3,28)$ | 119.993 | $\mathrm{D}(2,1,10,11)$ | -89.9606 |
| 10. | $\mathrm{R}(5,6)$ | 1.3951 | $\mathrm{~A}(3,4,5)$ | 119.994 | $\mathrm{D}(2,1,10,12)$ | 90.0394 |
| 11. | $\mathrm{R}(5,8)$ | 1.0998 | $\mathrm{~A}(3,4,13)$ | 119.9811 | $\mathrm{D}(6,1,10,11)$ | 90.0341 |
| 12. | $\mathrm{R}(6,9)$ | 1.0996 | $\mathrm{~A}(5,4,13)$ | 120.0249 | $\mathrm{D}(6,1,10,12)$ | -89.9659 |
| 13. | $\mathrm{R}(10,11)$ | 1.07 | $\mathrm{~A}(4,5,6)$ | 120.0047 | $\mathrm{D}(1,2,3,4)$ | -0.0568 |
| 14. | $\mathrm{R}(10,12)$ | 1.2584 | $\mathrm{~A}(4,5,8)$ | 120.0113 | $\mathrm{D}(1,2,3,28)$ | 179.9619 |
| 15. | $\mathrm{R}(13,14)$ | 1.43 | $\mathrm{~A}(6,5,8)$ | 119.984 | $\mathrm{D}(7,2,3,4)$ | -179.9777 |
| 16. | $\mathrm{R}(14,15)$ | 1.07 | $\mathrm{~A}(1,6,5)$ | 120.0 | $\mathrm{D}(7,2,3,28)$ | 0.041 |
| 17. | $\mathrm{R}(14,16)$ | 1.07 | $\mathrm{~A}(1,6,9)$ | 120.008 | $\mathrm{D}(2,3,4,5)$ | 0.0341 |
| 18. | $\mathrm{R}(14,17)$ | 1.54 | $\mathrm{~A}(5,6,9)$ | 119.992 | $\mathrm{D}(2,3,4,13)$ | -179.9964 |
| 19. | $\mathrm{R}(17,18)$ | 1.3952 | $\mathrm{~A}(1,10,11)$ | 119.8865 | $\mathrm{D}(28,3,4,5)$ | -179.9846 |
| 20. | $\mathrm{R}(17,19)$ | 1.3948 | $\mathrm{~A}(1,10,12)$ | 120.2269 | $\mathrm{D}(28,3,4,13)$ | -0.0151 |
| 21. | $\mathrm{R}(18,20)$ | 1.3947 | $\mathrm{~A}(11,10,12)$ | 119.8865 | $\mathrm{D}(2,3,28,29)$ | -61.5726 |
| 22. | $\mathrm{R}(18,21)$ | 1.0997 | $\mathrm{~A}(4,13,14)$ | 109.5 | $\mathrm{D}(4,3,28,29)$ | 118.4461 |
| 23. | $\mathrm{R}(19,22)$ | 1.3951 | $\mathrm{~A}(13,14,15)$ | 109.4712 | $\mathrm{D}(3,4,5,6)$ | 0.0131 |
| 24. | $\mathrm{R}(19,23)$ | 1.0996 | $\mathrm{~A}(13,14,16)$ | 109.4712 | $\mathrm{D}(3,4,5,8)$ | -179.9995 |
| 25. | $\mathrm{R}(20,24)$ | 1.3954 | $\mathrm{~A}(13,14,17)$ | 109.4712 | $\mathrm{D}(13,4,5,6)$ | -179.9563 |
| 26. | $\mathrm{R}(20,25)$ | 1.0997 | $\mathrm{~A}(15,14,16)$ | 109.4712 | $\mathrm{D}(13,4,5,8)$ | 0.0311 |
| 27. | $\mathrm{R}(22,24)$ | 1.3948 | $\mathrm{~A}(15,14,17)$ | 109.4713 | $\mathrm{D}(3,4,13,14)$ | 90.1178 |
| 28. | $\mathrm{R}(22,26)$ | 1.0998 | $\mathrm{~A}(16,14,17)$ | 109.4712 | $\mathrm{D}(5,4,13,14)$ | -89.9127 |
| 29. | $\mathrm{R}(24,27)$ | 1.0997 | $\mathrm{~A}(14,17,18)$ | 119.9972 | $\mathrm{D}(4,5,6,1)$ | -0.0376 |
| 30. | $\mathrm{R}(28,29)$ | 1.43 | $\mathrm{~A}(14,17,19)$ | 120.0043 | $\mathrm{D}(4,5,6,9)$ | 179.9881 |
| 31. | $\mathrm{R}(29,30)$ | 1.07 | $\mathrm{~A}(18,17,19)$ | 119.9985 | $\mathrm{D}(8,5,6,1)$ | 179.975 |
|  |  |  |  |  |  |  |

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| 32. | R(29,31) | 1.07 | A(17,18,20) | 120.0086 | $\mathrm{D}(8,5,6,9)$ | 0.0007 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 33. | R(29,32) | 1.07 | A(17,18,21) | 119.9808 | $\mathrm{D}(4,13,14,15)$ | -179.9071 |
| 34. |  |  | A(20,18,21) | 120.0106 | $\mathrm{D}(4,13,14,16)$ | 60.0929 |
| 35. |  |  | A(17,19,22) | 120.0 | $\mathrm{D}(4,13,14,17)$ | -59.9071 |
| 36. |  |  | A(17,19,23) | 120.008 | $\mathrm{D}(13,14,17,18)$ | -57.8579 |
| 37. |  |  | A(22,19,23) | 119.992 | $\mathrm{D}(13,14,17,19)$ | 122.1368 |
| 38. |  |  | A(18,20,24) | 119.9942 | $\mathrm{D}(15,14,17,18)$ | 62.142 |
| 39. |  |  | A(18,20,25) | 120.0128 | $\mathrm{D}(15,14,17,19)$ | -117.8632 |
| 40. |  |  | A(24,20,25) | 119.993 | $\mathrm{D}(16,14,17,18)$ | -177.8579 |
| 41. |  |  | A(19,22,24) | 120.0047 | $\mathrm{D}(16,14,17,19)$ | 2.1368 |
| 42. |  |  | A(19,22,26) | 119.984 | $\mathrm{D}(14,17,18,20)$ | -179.9729 |
| 43. |  |  | A(24,22,26) | 120.0113 | $\mathrm{D}(14,17,18,21)$ | -0.052 |
| 44. |  |  | A(20,24,22) | 119.994 | $\mathrm{D}(19,17,18,20)$ | 0.0323 |
| 45. |  |  | A(20,24,27) | 119.9811 | $\mathrm{D}(19,17,18,21)$ | 179.9532 |
| 46. |  |  | A(22,24,27) | 120.0249 | $\mathrm{D}(14,17,19,22)$ | -179.9798 |
| 47. |  |  | A(3,28,29) | 109.5 | $\mathrm{D}(14,17,19,23)$ | -0.0056 |
| 48. |  |  | A(28,29,30) | 109.4712 | $\mathrm{D}(18,17,19,22)$ | 0.0149 |
| 49. |  |  | A(28,29,31) | 109.4712 | $\mathrm{D}(18,17,19,23)$ | 179.9892 |
| 50. |  |  | A(28,29,32) | 109.4712 | $\mathrm{D}(17,18,20,24)$ | -0.0568 |
| 51. |  |  | A(30,29,31) | 109.4713 | $\mathrm{D}(17,18,20,25)$ | 179.9619 |
| 52. |  |  | A(30,29,32) | 109.4712 | $\mathrm{D}(21,18,20,24)$ | -179.9777 |
| 53. |  |  | A(31,29,32) | 109.4712 | D (21,18,20,25) | 0.041 |
| 54. |  |  |  |  | $\mathrm{D}(17,19,22,24)$ | -0.0376 |
| 55. |  |  |  |  | $\mathrm{D}(17,19,22,26)$ | 179.975 |
| 56. |  |  |  |  | $\mathrm{D}(23,19,22,24)$ | 179.9881 |
| 57. |  |  |  |  | $\mathrm{D}(23,19,22,26)$ | 0.0007 |
| 58. |  |  |  |  | $\mathrm{D}(18,20,24,22)$ | 0.0341 |
| 59. |  |  |  |  | $\mathrm{D}(18,20,24,27)$ | -179.9964 |
| 60. |  |  |  |  | $\mathrm{D}(25,20,24,22)$ | -179.9846 |
| 61. |  |  |  |  | $\mathrm{D}(25,20,24,27)$ | -0.0151 |
| 62. |  |  |  |  | $\mathrm{D}(19,22,24,20)$ | 0.0131 |
| 63. |  |  |  |  | $\mathrm{D}(19,22,24,27)$ | -179.9563 |
| 64. |  |  |  |  | $\mathrm{D}(26,22,24,20)$ | -179.9995 |
| 65. |  |  |  |  | D (26,22,24,27) | 0.031 |
| 66. |  |  |  |  | $\mathrm{D}(3,28,29,30)$ | 82.8463 |
| 67. |  |  |  |  | $\mathrm{D}(3,28,29,31)$ | -157.1537 |
| 68. |  |  |  |  | $\mathrm{D}(3,28,29,32)$ | -37.1537 |

## B. Vibrational Spectra

A detailed study of vibrational spectra has been carried out of the reported compound BMB and its vibrational frequencies have been calculated using DFT-B3LYP level with $6-31++G(d, p)$, there is a good agreement between the observed frequencies and those calculated by the DFT comparative chart is shown in Table 2 in which experimental values of IR ( KBr and nuzol), FTIR and laser Raman are displayed and simultaneously compared with the calculated values, respective assignments are shown corresponding to the results.

| S.No | Calculated Frequencies |  |  | Experimental Frequencies |  |  |  | Assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Frequency | I R | Raman <br> Activity | Raman | $\mathrm{IR}(\mathrm{KBr})$ | IR(Nuzol) | FTIR |  |
| 1 | 17.09 | 0.0838 | 9.5624 |  |  |  |  |  |
| 2 | 37.56 | 0.6967 | 5.6534 | 40 |  |  |  |  |
| 3 | 64.03 | 1.1422 | 9.5906 |  | 56.25 |  |  |  |
| 4 | 77.57 | 5.2046 | 1.4154 | 75 |  |  |  |  |
| 5 | 114.22 | 6.2968 | 1.0163 | 114 |  |  |  |  |
| 6 | 152.91 | 6.6623 | 1.4414 | 154 |  |  |  |  |
| 7 | 165.13 | 2.3527 | 1.1883 | 169 |  |  |  |  |
| 8 | 171.78 | 1.1662 | 1.5369 |  |  |  |  |  |
| 9 | 195.96 | 2.5564 | 3.8082 |  |  |  |  |  |
| 10 | 215.01 | 3.5219 | 5.8225 |  |  |  |  |  |
| 11 | 258.98 | 1.3437 | 0.85 | 238 |  |  |  |  |
| 12 | 269.56 | 2.9908 | 1.8916 |  |  |  |  |  |
| 13 | 272.8 | 5.1187 | 2.4645 | 306 |  |  |  |  |
| 14 | 340.12 | 3.4819 | 3.3594 |  |  |  |  |  |
| 15 | 373.86 | 6.8729 | 1.1237 |  |  |  |  |  |
| 16 | 426.69 | 1.9839 | 2.9115 |  | 424 | 417 |  |  |
| 17 | 432.62 | 0.5018 | 1.5374 | 445 |  |  |  |  |
| 18 | 452.6 | 6.6319 | 1.4434 |  |  | 443 |  |  |
| 19 | 477.72 | 7.434 | 0.9989 |  | 487 |  |  |  |
| 20 | 514.01 | 6.5073 | 1.8561 |  |  |  |  |  |
| 21 | 540.9 | 2.9829 | 5.163 |  | 533 |  |  |  |
| 22 | 569.67 | 10.487 | 2.6541 | 571 | 562 |  | 562.9 |  |
| 23 | 609.4 | 15.4741 | 3.8565 | 608 | 590 |  |  |  |
| 24 | 634.98 | 6.6307 | 1.6844 |  |  |  |  |  |
| 25 | 644.46 | 25.4521 | 4.8084 |  |  |  |  |  |
| 26 | 659.33 | 0.546 | 5.3805 | 668 | 658 | 657 | 664.8 | Benzyloxy group vib. |
| 27 | 743.04 | 57.7397 | 7.5906 |  | 699 | 699 | 705.5 |  |
| 28 | 745.55 | 2.9784 | 11.2749 |  | 729 | 729 |  |  |
| 29 | 761.22 | 70.7589 | 2.0952 | 745 | 749 | 748 |  | Benzyloxy group vib. |
| 30 | 789.44 | 2.5475 | 9.8687 |  |  |  |  |  |
| 31 | 804.77 | 5.1078 | 1.2201 |  |  |  |  |  |

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| 32 | 813.47 | 3.2565 | 17.0797 | 815 | 814 | 813 | 817.5 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 33 | 865.34 | 39.3129 | 1.3033 | 864 | 857 | 856 |  |  |
| 34 | 887.54 | 0.4559 | 5.7387 |  | 867 | 867 |  |  |
| 35 | 955.7 | 3.8063 | 2.1931 |  | 920 | 919 |  |  |
| 36 | 965.03 | 12.4567 | 1.292 |  |  |  |  |  |
| 37 | 975.84 | 25.4283 | 3.3398 | 980 |  |  |  |  |
| 38 | 997.25 | 20.7786 | 3.2851 |  | 995 | 990 | 990.7 |  |
| 39 | 1008.69 | 57.4489 | 10.4585 | 1005 |  |  |  |  |
| 40 | 1023.98 | 4.3347 | 0.1458 | 1014 |  |  |  |  |
| 41 | 1036.71 | 7.1085 | 28.4108 |  | 1032 | 1032 |  |  |
| 42 | 1039.62 | 45.9348 | 11.3857 |  |  |  |  |  |
| 43 | 1042.32 | 36.0296 | 6.5537 | 1045 |  |  |  | C-H <br> deformaton |
| 44 | 1064.74 | 5.0209 | 1.3458 |  |  |  |  |  |
| 45 | 1073.87 | 2.1404 | 7.8017 |  |  |  |  |  |
| 46 | 1087.3 | 2.6381 | 2.4975 |  |  |  |  |  |
| 47 | 1126.33 | 6.8258 | 0.7527 |  |  |  | 1138.3 |  |
| 48 | 1160.63 | 223.9749 | 15.3457 | 1045 | 1160 | 1159 |  |  |
| 49 | 1162.31 | 12.583 | 9.1586 |  |  |  |  |  |
| 50 | 1187.86 | 11.2875 | 1.5374 |  |  |  |  |  |
| 51 | 1200.46 | 18.0193 | 8.3746 | 1207 |  |  |  |  |
| 52 | 1220.74 | 2.9392 | 8.4896 |  | 1237 | 1237 |  |  |
| 53 | 1231.31 | 0.1759 | 4.717 |  |  |  |  |  |
| 54 | 1242.59 | 52.266 | 3.0441 |  |  |  |  |  |
| 55 | 1251.33 | 15.8146 | 8.2501 | 1252 | 1262 | 1261 | 1265.6 |  |
| 56 | 1287.27 | 205.8154 | 31.6724 | 1272 | 1276 | 1276 |  |  |
| 57 | 1297.76 | 166.3352 | 29.8757 |  |  |  |  |  |
| 58 | 1311.22 | 21.0317 | 9.0126 |  |  |  |  |  |
| 59 | 1328.37 | 10.7704 | 3.433 |  |  |  |  |  |
| 60 | 1357.5 | 18.7576 | 34.5632 | 1360 | 1348 | 1348 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 61 | 1380.65 | 4.8473 | 13.8039 | 1396 | 1385 | 1380 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 62 | 1420.17 | 2.9607 | 3.3444 |  | 1401 | 1400 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 63 | 1426.19 | 50.7143 | 10.7557 | 1438 | 1426 | 1425 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 64 | 1463.89 | 57.6602 | 10.5604 | 1463 | 1466 | 1464 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |


| 65 | 1505.68 | 0.0824 | 11.7542 |  | 1506 | 1505 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 66 | 1509.28 | 18.7986 | 4.3621 |  |  |  | 1510 | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 67 | 1536.13 | 41.4531 | 25.8317 | 1521 |  |  |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 68 | 1548.45 | 110.4146 | 7.8764 |  |  |  |  |  |
| 69 | 1553.55 | 25.7719 | 3.0702 |  |  |  |  |  |
| 70 | 1555.79 | 11.4604 | 30.9381 |  |  |  |  |  |
| 71 | 1569.12 | 22.1381 | 26.8488 |  |  |  |  |  |
| 72 | 1607.8 | 55.618 | 27.1678 | 1596 | 1598 | 1597 |  | $\begin{array}{r} \mathrm{C}-\mathrm{C} \\ \text { stretching } \end{array}$ |
| 73 | 1618.84 | 13.6277 | 23.7543 |  |  |  |  |  |
| 74 | 1624.98 | 100.5387 | 213.6456 |  |  |  |  |  |
| 75 | 1638.63 | 3.3304 | 26.548 | 1678 | 1667 | 1673 | 1678.1 |  |
| 76 | 1709.16 | 129.7607 | 106.4191 | 1709 |  |  |  |  |
| 77 | 2919.55 | 156.1254 | 154.4829 | 2853 | 2840 | 2854 | 2849.2 | C-H <br> stretching |
| 78 | 3037.79 | 31.6419 | 94.3443 | 2964 | 2950 | 2926 |  |  |
| 79 | 3060.49 | 25.7204 | 91.2246 | 3025 | 3013 |  |  | $\begin{array}{r} \mathrm{C}-\mathrm{H} \\ \text { stretching } \end{array}$ |
| 80 | 3096.26 | 30.7167 | 49.2209 | 3076 | 3061 |  |  |  |
| 81 | 3109.18 | 15.9513 | 123.3103 |  |  |  |  |  |
| 82 | 3166.09 | 13.2202 | 91.7108 |  |  |  |  |  |
| 83 | 3174.09 | 7.7454 | 47.9705 |  |  |  |  |  |
| 84 | 3190.19 | 1.633 | 71.8359 |  |  |  |  |  |
| 85 | 3193.4 | 5.9949 | 64.6025 |  |  |  |  |  |
| 86 | 3200.91 | 23.6376 | 82.2171 |  | 3408 | 3450 |  |  |
| 87 | 3215.59 | 8.6848 | 129.8019 | 4100 | 3651 |  |  |  |
| 88 | 3225.19 | 25.563 | 134.344 |  |  |  |  |  |
| 89 | 3225.96 | 11.3977 | 109.43 |  |  |  |  |  |
| 90 | 3235.81 | 4.9312 | 49.0456 |  |  |  |  |  |

Raman Activity Spectrum



FIGURE 2

1) $C-H$ Vibrations: In substituted benzene rings, the C-H stretching vibrations give rise to bands at $3120-3000 \mathrm{~cm}-1$ [9]. In the present compound BMB these values are observed at $3025 \mathrm{~cm}^{-1}$ and $3076 \mathrm{~cm}^{-1}$ for Raman and $3013 \mathrm{~cm}^{-1}$ and $3061 \mathrm{~cm}^{-1}$ for $\operatorname{IR}(\mathrm{KBr})$. These values are in agreement with those obtained by DFT-B3LYP level with $6-31++\mathrm{G}(\mathrm{d}, \mathrm{p})$ which are $3060 \mathrm{~cm}^{-1}$ and $3096 \mathrm{~cm}^{-1}$. The in- plane aromatic C-H deformation vibrations occur in the region $1300-1000 \mathrm{~cm}-1 .[10]$ The vibrations at $1045 \mathrm{~cm}^{-1}$ for Raman $1160 \mathrm{~cm}^{-1}$ and $1159 \mathrm{~cm}^{-1}$ for IR ( KBr and nuzol respectively) and $1138.3 \mathrm{~cm}^{-1}$ for FTIR are in fair agreement with the calculated values i.e 1126,1160 and $1162 \mathrm{~cm}^{-1}$.
2) $C$ - C vibrations: The bands in the range $1400-1650 \mathrm{~cm}-1$ are generally assigned to C -C stretching mode .[11] The bands of variable intensity are generally observed at $1625-1590 \mathrm{~cm}-1,1590-1575 \mathrm{~cm}-1,1540-1470 \mathrm{~cm}-1,1465-1430 \mathrm{~cm}-1$ and $1380-$ $1280 \mathrm{~cm}-1$ from the frequency ranges given by Varsanyi.[12] In the present study the bands observed at $1360,1396,1438,1465$, $1521,1596 \mathrm{~cm}-1$ at Raman, 1348, 1385, 1401, 1426, 1466, 1506, $1598 \mathrm{~cm}-1$ at $\operatorname{IR}(\mathrm{KBr}), 1348,1380,1400,1425,1464,1505$, $1597 \mathrm{~cm}-1$ at IR (nuzol), and $1510 \mathrm{~cm}-1$ in FTIR are assigned to C-C stretching mode. These values are in in good agreement with the calculated values of the compound which comes out to be at $1420.17,1426.19,1463.89,1505.68,1536.13,1548.45$, $1553.55,1555.79,1569.12,1607.8,1618.84,1624.98 \mathrm{~cm}-1$.
3) Aldehyde group vibrations: The C-H stretching vibrations of the aldehyde group usually appear in the region 2871-2806 cm-1 [13]. These are observed $2853 \mathrm{~cm}-1$ in Raman and $2840 \mathrm{~cm}-1$ in IR ( KBr ) $2854 \mathrm{~cm}-1$ in IR (nuzol) is in agreement with the calculated value which is 2919.55 and the literature values. The carbonyl $\mathrm{C}=\mathrm{O}$ stretching vibrations in the substituted benzaldehydes are reported near $1700 \mathrm{~cm} \_1$ [13]. The bands cantered $1678.1 \mathrm{~cm}-1$ in FTIR, $1667 \mathrm{~cm}-1$ in IR (KBr) and 1673 (nuzol) and 1678 and $1709 \mathrm{~cm}-1$ in Raman for BMB is attributed to $\mathrm{C}=\mathrm{O}$ stretching vibration of the aldehyde group which shows fair agreement with the calculated value 1709.16. A weak-to-medium intensity band due to the aldehyde group CHO deformation vibration is found in the region $975-780 \mathrm{~cm}-1$ [13] . In agreement with this, the bands at $815,864,980 \mathrm{~cm}-1$ in Raman, $814,857,867,920 \mathrm{~cm}-1$ at $\operatorname{IR}(\mathrm{KBr}), 813,856,867,919 \mathrm{~cm}-1$ at $\operatorname{IR}$ (nuzol) could be assigned to CHO out of plane deformation for BMB. These values shows support to the calculated values which is in the same given range and for the compound BMB are 789.44, 804.77, 813.47, 865.34, 887.54, 955.7, $965.03,975.84 \mathrm{~cm}-1$.
4) Benzyloxy Group Vibrations: The vibrations in the range $745-730 \mathrm{~cm}-1$ and $700-695 \mathrm{~cm}-1$ attributes to benzyloxy group.[14] The vibrations at 745 and $668 \mathrm{~cm}-1$ at Raman, $749,729,699,658 \mathrm{~cm}-1$ for $\operatorname{IR}(\mathrm{KBr}), 657,699,729$ and $748 \mathrm{~cm}-1$ for $\operatorname{IR}$ (nuzol) and 664.8 and $705.5 \mathrm{~cm}-1$ for FTIR can be assigned to benzyloxy group. The calculated values for the same comes out to be $634.88,644.46,659.33,743.04,745.55 \mathrm{~cm}-1$. The experimental and the calculated values of frequency shows good agreement.

## C. Thermodynamic Properties

Theoretical geometrical parameters represent a good approximation and they are the basis for calculating vibrational frequencies and thermodynamic parameters. The frequency calculations compute the zero point energies, thermal correction to internal energy and entropy as well as the heat capacity for a molecular system. These functions describe the thermodynamic stability of the system at the given conditions of pressure and temperature.

| Zero-point correction | $=$ | 0.258469 (Hartree/Particle) |
| :--- | :--- | :---: |
| Thermal correction to Energy | $=$ | 0.273962 |
| Thermal correction to Enthalpy | $=$ | 0.274906 |
| Thermal correction to Gibbs Free Energy | $=$ | 0.213929 |
| Sum of electronic and zero-point Energies | $=$ | -800.984731 |
| Sum of electronic and thermal Energies | $=$ | -800.969239 |
| Sum of electronic and thermal Enthalpies | $=$ | -800.968295 |
| Sum of electronic and thermal Free Energies | $=$ | -801.029272 |

Table from calculation

|  | E <br> (Thermal) <br> KCal/Mol | CV <br> Cal/Mol- <br> Kelvin | S <br> Cal/Mol- <br> Kelvin |
| :--- | ---: | ---: | ---: |
| Total | 171.914 | 59.343 |  |$|$| 128.338 |
| ---: |
| Electronic |

Table 3

## D. Electric Moment

The dipole moment in a molecule is an important property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole-dipole interactions, because higher the dipole moment, stronger will be the intermolecular interactions. In the absence of experimental data, the values of polarizability and hyperpolarizability calculated at the same level of theory and the same basis set for the compound BMB, can provide a satisfactory comparison of these quantities.

Calculated dipole moment ( $\mu$, in Debye ), mean polarizabilit ( $\bar{\alpha}$, in a.u. ), anisotropy of polarizability ( $\Delta \alpha$, in a.u. ) and first hyperpolarizability ( $\beta$, in a.u. ) of BMB by DFT by B3LYP/6-31G(d,p).

| Dipole moment |  | Polarizability |  | Hyperpolarizability |  |
| :---: | :--- | :--- | :--- | :--- | :--- |
| $\mu_{\mathrm{x}}$ | 2.2399 | $\alpha_{\mathrm{xx}}$ | -115.0351 | $\beta_{\mathrm{xxx}}$ | 84.7803 |
| $\mu_{\mathrm{y}}$ | 0.9507 | $\alpha_{\mathrm{yy}}$ | -85.1199 | $\beta_{y y y}$ | -27.0337 |
| $\mu_{\mathrm{z}}$ | 0.4156 | $\alpha_{z z}$ | -109.3771 | $\beta_{z z z}$ | 5.1368 |
|  |  | $\alpha_{\mathrm{xy}}$ | 1.6480 | $\beta_{\mathrm{xyy}}$ | -19.5231 |
|  |  | $\alpha_{\mathrm{xz}}$ | -7.4247 | $\beta_{\mathrm{xxy}}$ | 30.2569 |
|  |  | $\alpha_{\mathrm{yz}}$ | 1.4067 | $\beta_{\mathrm{xxz}}$ | 14.5276 |
|  |  |  |  | $\beta_{\mathrm{xzz}}$ | 18.5722 |
|  |  |  |  | $\beta_{\mathrm{yzz}}$ | -2.0060 |
|  |  |  |  | $\beta_{\mathrm{yyz}}$ | 5.2307 |
|  |  |  |  | $\beta_{\mathrm{xyz}}$ | 22.3774 |

The component of dipole moment $\mu$, polarizability $\alpha$ and the first hyperpolarizability $\beta$ can be calculated by using the following equations
$\mu=\left(\mu_{x}{ }^{2}+\mu_{y}{ }^{2}+\mu_{z}{ }^{2}\right)^{1 / 2}$
$\bar{\alpha}=1 / 3\left(\alpha_{x x}+\alpha_{y y}+\alpha_{z z}\right)$
$\Delta \alpha=1 / \sqrt{ } 2\left\{\left[\left(\alpha_{x x}-\alpha_{y y}\right)^{2}+\left(\alpha_{y y}-\alpha_{z z}\right)^{2}+\left(\alpha_{z z}-\alpha_{x x}\right)^{2}+6 \alpha_{x z}^{2}\right]\right\}^{1 / 2}$
First order polarizability $\beta=\left[\left(\beta_{x x x}+\beta_{x y y}+\beta_{x z z}\right)^{2}+\left(\beta_{y y y}+\beta_{x x y}+\beta_{y z z}\right)^{2}+\left(\beta_{z z z}+\beta_{x x z}+\beta_{y y z}\right)^{2}\right]^{1 / 2}$
Using these equations values for the reported compound BMB comes out to be as follows....
$\mu=2.4866$
$\bar{\alpha}=103.1773$
$\Delta \alpha=30.3817$
$\beta=87.4535$

## v. CONCLUSION

In the present work we have calculated the geometric parameters, the vibrational frequencies and NLO properties of 4-benzyloxy-3-methoxy-benzaldehy by using Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G (DP) basis and compared these values with the experimentally recorded FTIR, IR ( KBr and nuzol) and Raman spectra. In general, a good agreement between experimental and calculated normal modes of vibrations have been observed. We also calculated thermodynamic properties as heat capacity, entropy, enthalpy and Gibb's free energy of the titled compounds at different temperatures along with dipole moment, polarisability and hyperpolarisability .

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