

Vibrational Spectra, Structural Confirmations and Intramolecular Charge Transfer of 4-methyl-3-Nitrobenzaldehyde by Density Functional Theory

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Abstract—In this study we present a comparative analysis on experimental and abinitio DFT calculations on 4-methyl-3-nitrobenzaldehyde (further referred as 4,3MNB). The molecular geometry, harmonic vibrational frequencies, thermodynamic properties, frontier molecular orbitals analysis for the reported compound in ground state were obtained by density functional theory (DFT) with the help of Gaussian 09 program package with standard B3LYP/6-311++G(d,p) basis set combination. The results of the calculations were applied to simulated infrared and Raman spectra of the reported compound, which showed good agreement with the observed spectra. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule.

Key words DFT calculations, 4-methyl-3-nitrobenzaldehyde, thermodynamic properties, frontier molecular orbitals, Gaussian 09, B3LYP.

Introduction

Benzaldehydes and its derivatives are one of the simplest in aromatic aldehydes and are known as bitter almond, it has many other uses such as in manufacturing of dyes, perfumes, flavorings, cinnamic and mandelic acids, and it is also used as a solvent[1]. It is synthesized in laboratories from toluene being chlorinated to benzyl chloride or by direct oxidation of toluene with manganese dioxide. Some of the developments in the use of benzaldehyde are for the health and agriculture industries. Benzaldehyde is being used as a pesticide and also as an anticancer agent and have shown anti tumour activity in mice.[2] It is used as a bee repellent in the harvesting of honey. These uses are still in development but would be very helpful in solving some of these problems of today. The benzaldehyde and its derivatives have received attention because of their chemical and biological importance. The benzaldehyde

and substituted benzaldehydes have been subjected to various spectroscopic studies [3-7].

Experimental and Computational The infrared spectra of the compound 4,3-MNB was recorded on Perkin-Elmer M-683 spectrophotometer in the region 400-4000 cm^{-1} using KBr pellets and nujolmull solvent. The laser Raman spectrum in the region 40-4300 cm^{-1} was recorded on “Spex Rama Lab” spectrophotometer using 52 mg argon-krypton laser beam of wavelength 488 nm.[8]

Whereas All the calculations were carried out for 4,3-MNB with Gaussian 09W program package [9] using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G(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.

MOLECULAR STRUCTURE: The molecular structure of the mentioned compound 4,3-MNB 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++G (d) and 6-311++G (d,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. [10]

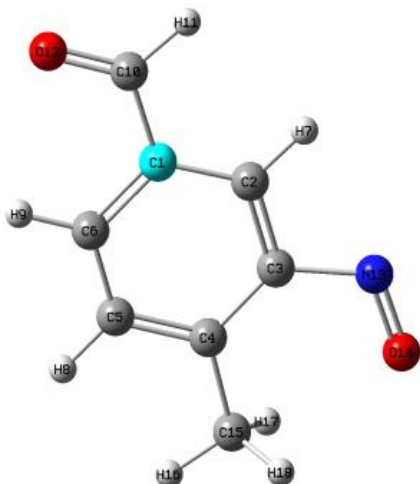


Figure 1

Table 1: Calculated Optimized Geometrical Parameters of 4,3-MNB, at B3LYP/6-31G(d,p): bond length (Å), bond angle(°), dihedral angles(°)

S. No	Atoms of molecule	Bond length (Å)	Angle between atoms (°)	Bond angle (°)	Dihedral angle between atoms (°)	Dihedral angle (°)
1.	R(1,2)	1.3952	A(2,1,6)	119.9985	D(6,1,2,3)	0.0323
2.	R(1,6)	1.3948	A(2,1,10)	119.9972	D(6,1,2,7)	179.9532
3.	R(1,10)	1.54	A(6,1,10)	120.0043	D(10,1,2,3)	-179.9729
4.	R(2,3)	1.3947	A(1,2,3)	120.0086	D(10,1,2,7)	-0.052
5.	R(2,7)	1.0997	A(1,2,7)	119.9808	D(2,1,6,5)	0.0149
6.	R(3,4)	1.3954	A(3,2,7)	120.0106	D(2,1,6,9)	179.9892
7.	R(3,13)	1.47	A(2,3,4)	119.9942	D(10,1,6,5)	-179.9798
8.	R(4,5)	1.3948	A(2,3,13)	120.0128	D(10,1,6,9)	-0.0056
9.	R(4,15)	1.54	A(4,3,13)	119.993	D(2,1,10,11)	-89.9606
10.	R(5,6)	1.3951	A(3,4,5)	119.994	D(2,1,10,12)	90.0394
11.	R(5,8)	1.0998	A(3,4,15)	119.9811	D(6,1,10,11)	90.0341
12.	R(6,9)	1.0996	A(5,4,15)	120.0249	D(6,1,10,12)	-89.9659
13.	R(10,11)	1.07	A(4,5,6)	120.0047	D(1,2,3,4)	-0.0568
14.	R(10,12)	1.2584	A(4,5,8)	120.0113	D(1,2,3,13)	179.9619
15.	R(13,14)	1.1968	A(6,5,8)	119.984	D(7,2,3,4)	-179.9777
16.	R(15,16)	1.07	A(1,6,5)	120.0	D(7,2,3,13)	0.041
17.	R(15,17)	1.07	A(1,6,9)	120.008	D(2,3,4,5)	0.0341
18.	R(15,18)	1.07	A(5,6,9)	119.992	D(2,3,4,15)	-179.9964
19.			A(1,10,11)	119.8865	D(13,3,4,5)	-179.9846
20.			A(1,10,12)	120.2269	D(13,3,4,15)	-0.0151
21.			A(11,10,12)	119.8865	D(2,3,13,14)	121.1149

22.			A(3,13,14)	120.0	D(4,3,13,14)	-58.8665
23.			A(4,15,16)	119.4712	D(3,4,5,6)	0.0131
24.			A(4,15,17)	119.4712	D(3,4,5,8)	-179.9995
25.			A(4,15,18)	119.4712	D(15,4,5,6)	-179.9563
26.			A(16,15,17)	119.4713	D(15,4,5,8)	0.0311
27.			A(16,15,18)	119.4712	D(3,4,15,16)	-47.228
28.			A(17,15,18)	119.4712	D(3,4,15,17)	72.7721
29.					D(3,4,15,18)	-167.228
30.					D(5,4,15,16)	132.7415
31.					D(5,4,15,17)	-107.2585
32.					D(5,4,15,18)	12.7415
33.					D(4,5,6,1)	-0.0376
34.					D(4,5,6,9)	179.9881
35.					D(8,5,6,1)	179.975
36.					D(8,5,6,9)	0.0007

VIBRATIONAL SPECTRA A detailed study of vibrational spectra has been carried out of the reported compound 4,3-MNB and the 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), and laser Raman are displayed and simultaneously compared with the calculated values.

Table 2

S.No.	Experimental			Calculated	Assignments
	Raman	IR(KBr)	IR(nuzol)		
1.	160			177.90	α (C-CHO)
2.	220			235.25	α (C-NO ₂)
3.	280			290.69	β (C-NO ₂)
4.	328			332.45	α (C-CH ₃)
5.	371			380.24	β (C-CH ₃), β (C-CHO)
6.	407			398.27	α ring
7.			432	433.87	α ring
8.			586	598.55	β (C-CH ₃)
9.			607		β ring
10.	652		648	642.61	β ring
11.			691		α ring
12.	719	712	715	723.60	N ring breathing
13.	840	840			α (C-H)
14.		900	904	875.70	α (C-H)
15.	930	918	926	933.01	triagonal bending
16.	1030	1022	1027	1037.42	β (C-H)

17.	1080	1070	1077	1082.70	σ (C-NO ₂)
18.		1130		1098.01	β (C-H)
19.	1176		1169		σ (C-CH ₃)
20.	1226		1214	1212.28	σ (C-CHO)
21.		1300		1316.82	
22.		1457	1457	1450.31	σ ring
23.		1522	1530	1538.09	σ ring
24.	1590			1582.95	σ ring
25.	1630	1618	1627	1639.04	σ ring
26.		3003		3066.25	σ (C-H) aromatic
27.	3091		3089		σ (C-H) aromatic
28.		3102		3120.55	σ (C-H) aromatic
29.				3200.13	
30.				3219.87	

Where α is out of plane bending, β in plane bending and σ is stretching.

C-H VIBRATIONS The compound for study 4,3-MNB is a trisubstituted benzene, therefore only three hydrogen atoms are left around the ring. As such three C-H valence oscillations are expected in the region 3000-3100 cm⁻¹. Thus, the three ring C-H stretching modes are well assigned at 3003 cm⁻¹(KBr), 3089 (nuzol)/3091 cm⁻¹ (Raman) and 3102 cm⁻¹ (KBr). These assignments are in good agreement with the literature values [11-13]. These values find good agreement with DFT calculated values at 3066.25 cm⁻¹ and 3120.55 cm⁻¹.

C-C VIBRATIONS In substituted benzene bands are usually observed in the region 1400-1650 cm⁻¹. The bands at 1590 cm⁻¹ and 1630 cm⁻¹ have been clearly identified as the components corresponding C-C vibrations of benzene and these values corresponds to calculated values 1582.95 cm⁻¹ and 1639.04 cm⁻¹.

NO₂ GROUP VIBRATIONS In the reported compound the frequency 1522 cm⁻¹ for IR(KBr) and 1530 cm⁻¹ for IR(nuzol) with 1590 cm⁻¹ for Raman is assigned to NO₂ symmetric stretching vibration, the calculated values for the same is 1538.09 cm⁻¹ and 1582.95 cm⁻¹, these values are in fair agreement with the reported literature value.[15,16] Many workers have reported NO₂ deformation bond in the range 825-890 cm⁻¹ [17,18], in our study the values at 840 cm⁻¹ for Raman and 900 cm⁻¹ and 904 cm⁻¹ for IR (KBr and nuzol respectively are assigned to this mode which is in good agreement with the calculated values i.e. 875.70 cm⁻¹.

CHO GROUP VIBRATIONS The C=O in-plane bending vibration is observed in the region 800-860 cm⁻¹ in many of the substituted benzaldehydes. The strong band observed at 840 cm⁻¹ may be assigned to this vibration. The C-H in-plane bending is identified near 1400 cm⁻¹ in a number of substituted benzaldehydes. This mode is assigned at 1330 cm⁻¹ in the present study, which is in agreement with the calculated value 1316.82 cm⁻¹. Green and Harrison[19] and Furushima[20] assigned the torsional mode of aldehydic group at 113 and 110 cm⁻¹ in benzaldehyde and p-hydroxy benzaldehyde. In the present study this mode has been assigned at 160 cm⁻¹ for Raman and 177.90 for calculated value.

FRONTIER MOLECULAR ORBITALS The electronic absorption describes the transition from the ground state to the first excited state and is explained as one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The following figures 2 and 3 shows the HOMO and LUMO levels. The HOMO level is at -0.2242 a.u. and LUMO at -0.1119 a.u. and the difference between the two levels is 0.1123 a.u. which indicates a better stability of the compound.

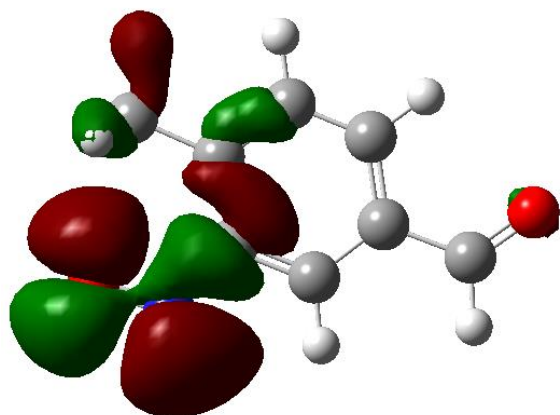


Figure 2

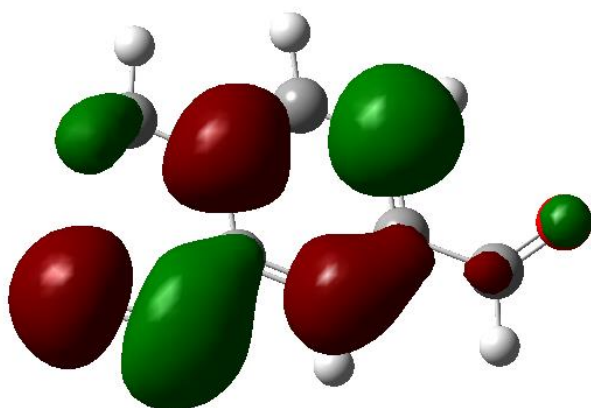


Figure 3

MOLECULAR ELECTROSTATIC POTENTIAL

The molecular electrostatic potential (MESP) is a pictorial representation of electrostatic potential shown on a constant electron density surface and it at the same time exhibits the molecular parameters as shape, size and electrostatic potential value represented in terms of colour coding. The different set of values of the electrostatic potential on the surface can be denoted by different colours as red colour depicts the region of the most electro-negative electrostatic potential, blue the region of the most electro-positive electrostatic potential, green the region of zero potential and yellow slightly electron rich region. This method represents the charge density on a molecule in a glance. In case of our reported compound the molecular electrostatic potential obtained by B3LYP/6-311++G(d,p) is shown in figure 4. In our compound we can summarise that the existence of green region in the ring surfaces and methoxy group corresponds to a potential centre between the red and blue colour which are two extremes.

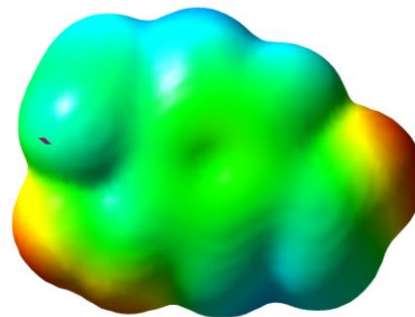


Figure 4

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