

Structural, Electronic, Optical and Vibrational properties of 2, 5-Dimethoxybenzotrile using Density Functional Theory

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Benzonitrile (BN) is polar solvent with a dipole moment of 4.18 D, and for this reason it has been extensively used in chemistry as a solvent. So we have done a vibrational spectroscopic investigation on 2, 5-Dimethoxybenzotrile which is a derivative of benzonitrile. The optimized geometry of the 2, 5-Dimethoxybenzotrile molecule has been determined by the method of density functional theory (DFT). For both geometry and total energy, it has been combined with B3LYP functional having 6-311 g (d, p) as the basis set. Using this optimized structure, we have calculated the infrared wave numbers, which are very useful in absence of experimental data. On Based on these results, we have discussed the correlation between the vibrational modes and the crystalline structure of 2, 5-Dimethoxybenzotrile. A complete assignment is provided for the observed FTIR spectra.

15 Introduction

The chemical origin of life was recognized almost two hundred years ago. The initial formulation of the concept that life is based on morphological units known as cells is generally attributed to a work by Schleiden and Schwann in 1838 [1]. Originally, it was
20 thought that only living beings could produce the molecules of life, so called organic molecules. Ten years before Schleiden and Schwann, in 1828, Wohler published a paper about the synthesis of urea, demonstrating that organic compounds can be created artificially. About the same time, Payen discovered the first
25 enzyme, diastase (a-, b-, or g-amylase). Eduard Buchner contributed the first demonstration of a complex biochemical process outside of a cell in 1897: alcoholic fermentation in cell extracts of yeast [2]. Benzonitrile (BN) is an aprotic polar solvent with a dipole moment of 4.18 D, and for this reason it has been
30 extensively used in chemistry as solvent [3]. As other applications, we can mention that BN has been employed as enriched precursor for the introduction of isotopes into l-tyrosine [4] and has been used in the electrochemical preparation of polydidodecy terthiophenes from a mixture of acetonitrile and
35 BN [5]. Cyanide compounds can be degraded by the *Pseudomonas* species [6], and BN is biotransformed directly to benzoic acid by the nitrilase enzyme or by several bacterium [7], or biotransformed to benzohydroxamic acid by the *Rhodococcus* rhodochrous bacterium [8].
40 As a part of our ongoing research work [9-20], here, the main objective of the present study is to investigate in detail the vibrational spectra of the important biological molecule i.e. 2, 5-Dimethoxybenzotrile.

Computational details

45 Initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface. The gradient corrected density functional theory (DFT) with the three-parameter hybrid

functional (B3) [21] for the exchange part and the Lee-Yang-Parr
50 (LYP) correlation function [22] has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, and energies of the optimized structures, using GAUSSIAN 09 [23]. The calculated vibrational frequencies have also been scaled by a factor of 0.963 [24]. By combining the
55 results of GaussView's program [25] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. We used this approach for the prediction of IR frequencies of title compound and found it to be very straightforward. Density functional theory calculations are
60 reported to provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for anharmonicity. A number of studies have been carried out regarding calculations of vibrational spectra by
65 using B3LYP methods with LANL2DZ and 6-311 G (d, p) basis sets. The scaling factor was applied successfully for B3LYP method and was found to be easily transferable in a number of molecules.

Results and discussion

70 The optimized Structure parameters of 2, 5-Dimethoxybenzotrile calculated by B3LYP method with the 6-311G (d, p) basis set are listed in Table 1 and are in accordance with the atom numbering scheme as shown in Figure 1. After geometry optimization local minimum energy obtained for
75 structured optimization of 2,5-Dimethoxybenzotrile with 6-311G (d, p) basis set is approximately -553.6768 (a.u.). The optimized bond parameters of molecule calculated by various methods are listed in Table 1.

The (C-C) bond length varies between the values 1.391Å-
80 1.414Å, while (C-O) bond length varies between 1.35Å- 1.421Å. (C-H) bond length varies between 1.081Å- 1.096Å while (C-N) bond length is 1.155Å in title molecule. All the calculated bond lengths are in good agreement with experimental data as given in

Table 1. The (C-C-C) bond angle varies from 118.5- 120.8 while (C-C-O) varies between 115.7- 125.3. The (C-C-H) bond angle varies between 118.5- 120.9. All the calculated bond angles are also in good agreement with experimental data as given in Table 1.

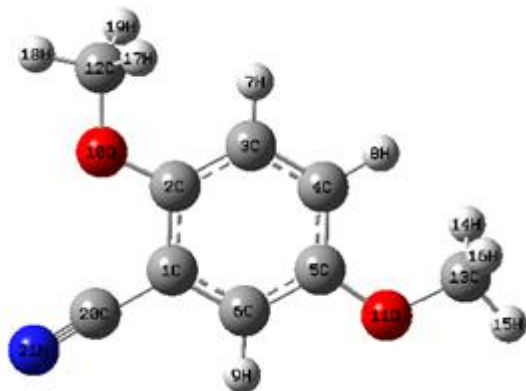


Figure 1 Model molecular structure of 2, 5-Dimethoxybenzonitrile

Atomic charge, Polarizability, Hyper Polarizability and Thermodynamic Properties

The Mullikan atomic charges for all the atoms of the 2, 5-Dimethoxybenzonitrile is calculated by B3LYP method with 6-311G (d, p) as basis set in gas phase and are presented in Table 2. Dipole moment (μ), polarizability $\langle\alpha\rangle$ and total first static hyperpolarizability β [26, 27] are also calculated (In Table 3) by using density functional theory. They can be expressed in terms of x, y, z components and are given by following equations 1, 2 and 3,

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (1)$$

$$\langle\alpha\rangle = 1/3 [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \quad (2)$$

$$\beta_{\text{Total}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (3)$$

The β components of Gaussian output are reported in atomic units, where 1 a.u. = 8.3693×10^{-33} e.s.u.

For 2, 5-Dimethoxybenzonitrile, the calculated value of dipole moment is 6.6832 Debye. Having higher dipole moment than water (2.16 Debye), 2, 5-Dimethoxybenzonitrile can be used as better solvent. As we see a greater contribution of α_{yy} in molecule which shows that molecule is elongated more towards Y direction and more contracted to X direction. Perpendicular part Z contributes less part of polarizability of molecule. β_{xxy}, β_{xxx} contribute larger part of hyperpolarizability in the molecule. This shows that XY plane and X-axis more optical active in these direction.

Several calculated thermodynamic properties based on the vibrational analysis at B3LYP and 6-311G (d, p) level, like internal thermal energy (E), constant volume heat capacity (C_v), and entropy (S), have been calculated and listed in Table 4. At the room temperature, conduction band is almost empty so electronic contribution in total energy negligible. Thermodynamic parameters clearly indicate that vibration motion plays a crucial role in assessing thermo dynamical behavior of title compounds.

Table 1 Bond Length (Å) and Bond Angle ($^\circ$) of 2, 5-Dimethoxybenzonitrile

Parameter	Experimental value	Calculated value
C ₁ -C ₂	1.404	1.414
C ₁ -C ₆	1.391	1.393
C ₁ -C ₂₀	1.439	1.428
C ₂ -C ₃	1.384	1.391
C ₂ -O ₁₀	1.361	1.355
C ₃ -C ₄	1.395	1.398
C ₃ -H ₇	0.950	1.081
C ₄ -C ₅	1.389	1.394
C ₄ -H ₈	0.950	1.081
C ₅ -C ₆	1.390	1.396
C ₅ -O ₁₁	1.670	1.363
C ₆ -H ₉	0.950	1.082
O ₁₀ -C ₁₂	1.438	1.421
O ₁₁ -C ₁₃	1.437	1.420
C ₁₂ -H ₁₇	0.980	1.095
C ₁₂ -H ₁₈	0.980	1.088
C ₁₂ -H ₁₉	0.980	1.095
C ₁₃ -H ₁₄	0.980	1.096
C ₁₃ -H ₁₅	0.980	1.088
C ₁₃ -H ₁₆	0.980	1.096
C ₂₀ -N ₂₁	1.149	1.155
C ₂ -C ₁ -C ₆	120.6	120.2
C ₂ -C ₁ -C ₂₀	119.9	119.9
C ₆ -C ₁ -C ₂₀	119.4	119.7
C ₁ -C ₂ -C ₃	118.6	118.5
C ₁ -C ₂ -O ₁₀	115.7	116.0
C ₃ -C ₂ -O ₁₀	115.5	125.3
C ₂ -C ₃ -C ₄	120.7	120.8
C ₂ -C ₃ -H ₇	119.6	120.4
C ₄ -C ₃ -H ₇	119.6	118.7
C ₃ -C ₄ -C ₅	120.3	120.5
C ₃ -C ₄ -H ₈	119.8	118.5
C ₅ -C ₄ -H ₈	119.8	120.9
C ₄ -C ₅ -C ₆	119.4	119.0
C ₄ -C ₅ -O ₁₁	125.0	125.1
C ₆ -C ₅ -O ₁₁	115.5	115.7
C ₁ -C ₆ -C ₅	120.1	120.6
C ₁ -C ₆ -H ₉	119.9	120.2
C ₅ -C ₆ -H ₉	119.9	119.0
C ₂ -O ₁₀ -C ₁₂	117.1	118.7
C ₅ -O ₁₁ -C ₁₃	117.3	118.3
O ₁₀ -C ₁₂ -H ₁₇	109.5	111.3
O ₁₀ -C ₁₂ -H ₁₈	109.5	105.6
O ₁₀ -C ₁₂ -H ₁₉	109.5	111.3
H ₁₇ -C ₁₂ -H ₁₈	109.5	104.3
H ₁₇ -C ₁₂ -H ₁₉	109.5	109.6
H ₁₈ -C ₁₂ -H ₁₉	109.5	109.3
O ₁₁ -C ₁₃ -H ₁₄	109.5	111.5
O ₁₁ -C ₁₃ -H ₁₅	109.5	105.4
O ₁₁ -C ₁₃ -H ₁₆	109.5	111.5
H ₁₄ -C ₁₃ -H ₁₅	109.5	109.2
H ₁₄ -C ₁₃ -H ₁₆	109.5	109.4
H ₁₅ -C ₁₃ -H ₁₆	109.5	109.2

Table 2 Mullikan Atomic Charges of 2, 5-Dimethoxybenzonitrile

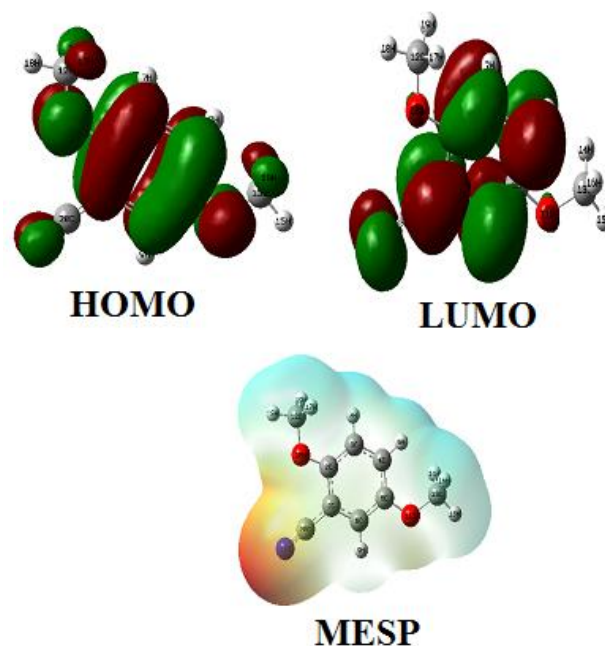
S. No.	Atom	Atomic charge
1.	C	-0.072937
2.	C	0.214282
3.	C	-0.131031
4.	C	-0.115976
5.	C	0.169725
6.	C	-0.023316
7.	H	0.111558
8.	H	0.111304
9.	H	0.115641
10.	O	-0.339320
11.	O	-0.350237
12.	C	-0.136676
13.	C	-0.134445
14.	H	0.111226
15.	H	0.134375
16.	H	0.111249
17.	H	0.113375
18.	H	0.140052
19.	H	0.113383
20.	C	0.079038
21.	N	-0.221272

Table 3 Polarizability and Hyper polarizability of 2,5-Dimethoxybenzonitrile

S. No.	Parameter	Polarizability
1.	α_{xx}	-64.5936
2.	α_{yy}	-72.3467
3.	α_{zz}	-71.7911
4.	α_{xy}	-11.1324
5.	α_{xz}	-0.0103
6.	α_{yz}	0.0003
α		69.5771
S. No.	Parameter	Hyper polarizability
1.	β_{xxx}	-55.2003
2.	β_{yyy}	-49.4907
3.	β_{zzz}	0.0027
4.	β_{xyy}	-21.3495
5.	β_{xxy}	-59.2675
6.	β_{xxz}	0.00309
7.	β_{xzz}	0.0232
8.	β_{yzz}	-1.2037
9.	β_{yyz}	-0.0063
10.	β_{xyz}	-0.0088
β		133.9699

Table 4 Thermodynamic Properties of 2, 5-Dimethoxybenzonitrile

Parameter	E (kcal/mol)	Cv (Cal/mol-K)	S (Cal/mol-K)
Total	109.696	41.681	104.291
Translational	0.889	2.981	41.176
Rotational	0.889	2.981	30.980
Vibrational	107.919	35.720	32.135

**Figure 2** HOMO, LUMO and MESP pictures of 2, 5-Dimethoxybenzonitrile**Electronic Properties**

The interaction with other species in a chemical system is also determined by frontier orbitals, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gap helps to distinguish the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gap is more polarized having reactive part as far as reaction is concerted [28]. The frontier orbital gap is 4.65 eV for 2,5-Dimethoxybenzonitrile given in Table 5.

The contour plots of the HOMO, LUMO and MESP of the molecule are shown in Figure 2. The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative, and neutral electrostatic potential region in terms of grading and is very useful in the investigation of molecular structure with its physiochemical property relationship [29, 30].

Table 5 Total Energy, HOMO, LUMO, Energy Gap and Dipole Moment of 2, 5-Dimethoxybenzonitrile

S. No.	Parameter	Value
1.	Total Energy E (a.u.)	-553.6768
2.	HOMO (a.u.)	-0.22488
3.	LUMO (a.u.)	-0.05405
4.	Frontier Orbital Energy Gap (4.646576 eV)	0.17083
5.	Dipole Moment (Debye)	6.6832

Assignment of fundamentals

2, 5-Dimethoxybenzonitrile has 21 atoms 57 normal modes of vibration. We made a reliable one-to-one correspondence between the fundamentals and the frequencies calculated by DFT

(B3LYP). The relative band intensities are also very satisfactory along with their positions. Some important modes are discussed

hereafter. The harmonic- vibration frequencies are calculated for the title molecule, and are given in Table 6.

5 **Table 6** Calculated Wave Numbers and its respective IR intensity of 2, 5-Dimethoxybenzonitrile

S. No.	Frequency	IR intensity	Vibrational assignments
1.	66	2.452	Out of plane Banding in both CH ₃
2.	84	0.067	Out of plane Banding in both CH ₃
3.	114	0.067	Twist in both CH ₃
4.	127	2.831	$\beta(C_1-C_{20}-N_{21})$
5.	171	7.659	$\tau(C_6-C_5-O_{11}-C_{13})$
6.	178	0.782	Butterfly Motion
7.	226	0.003	Twist in both CH ₃
8.	250	1.440	Twist in both CH ₃
9.	278	7.669	Ring Torsion
10.	353	2.086	Ring Breathing
11.	361	0.291	Twist in (C ₂₀ -N ₂₁)
12.	402	0.436	Twist in (C ₂₀ -N ₂₁)
13.	431	1.642	Ring Torsion
14.	442	0.928	$\tau(N_{21}-C_{20}-C_1-C_6)$
15.	491	9.550	Twist in (C ₂₀ -N ₂₁)
16.	539	1.773	Twist in both CH ₃
17.	608	0.716	Twist in (C ₂₀ -N ₂₁)
18.	625	3.559	Twist in whole Ring
19.	691	22.07	Ring Breathing
20.	716	0.216	$\tau(H_9-C_6-C_1-C_2)+\tau(C_5-C_4-C_3-H_7)$
21.	736	17.06	Ring Breathing
22.	792	43.47	Out of plane Banding(C ₃ -H ₇) & (C ₄ -H ₈)
23.	867	16.76	Twist in(C ₂₀ -N ₂₁)+ Out of plane Banding(C ₆ -H ₉)
24.	896	2.500	Ring Deformation
25.	897	1.491	Out of plane Banding (C ₄ -H ₈)+(C ₃ -H ₇)
26.	1010	52.92	Ring Breathing
27.	1038	82.01	$\nu(C_{13}-O_{11})+\nu(C_{12}-O_{10})$
28.	1104	38.07	$\omega(C_6-H_9)+\omega(C_4-H_8)$
29.	1128	0.242	Twist in both CH ₃
30.	1128	1.305	Twist in both CH ₃
31.	1138	40.82	$\omega(C_3-H_7)$
32.	1162	11.22	Scissoring in CH ₃ near O ₁₀
33.	1167	10.05	$\omega(C_3-H_7)+\omega(H_8-C_4)$ & Twist in CH ₃ near O ₁₁
34.	1210	204.1	$\omega(C_6-H_9)$
35.	1249	82.76	$\nu(C_3-C_4)$ & $\omega(C_3-H_7)$
36.	1259	136.9	$\omega(C_4-H_8)+\omega(C_6-H_9)$
37.	1296	60.97	Ring Deformation
38.	1397	71.89	$\omega(C_4-H_8)$ & $\nu(C-C)$ in hole molecule
39.	1422	25.04	$\omega(C_3-H_7)$
40.	1427	2.882	Scissoring in both CH ₃ group.
41.	1438	0.399	$\beta(H_{18}-C_{12}-H_{19})+\beta(H_{14}-C_{13}-H_{15})$
42.	1438	17.15	$\beta(H_{16}-C_{13}-H_{15})+\beta(H_{17}-C_{12}-H_{18})$
43.	1447	90.60	$\beta(H_{19}-C_{12}-H_{17})$
44.	1451	8.830	$\beta(H_{17}-C_{12}-H_{19})$
45.	1477	211.1	$\beta(H_{14}-C_{13}-H_{16})$
46.	1556	46.89	Ring Deformation
47.	1596	3.011	Ring Deformation
48.	2254	30.47	$\nu(C_{20}-N_{21})$
49.	2888	51.72	$\nu(C_{13}-H_{14})+\nu(C_{13}-H_{15})+\nu(C_{13}-H_{16})$
50.	2894	54.84	$\nu(C_{12}-H_{17})+\nu(C_{12}-H_{18})+\nu(C_{12}-H_{19})$
51.	2943	42.79	$\nu(C_{13}-H_{16})+\nu(C_{13}-H_{17})$
52.	2951	39.92	$\nu(C_{12}-H_{17})+\nu(C_{12}-H_{19})$
53.	3020	21.87	$\nu(C_{13}-H_{15})$
54.	3027	15.39	$\nu(C_{12}-H_{18})$
55.	3080	8.960	$\nu(C_3-H_7)+\nu(C_4-H_8)$
56.	3089	0.134	$\nu(C_6-H_9)$
57.	3094	3.686	$\nu(C_4-H_8)+\nu(C_3-H_7)$

Vibrational Modes Description

Spectral region above 2800 cm⁻¹:

The C-H stretching vibrations are generally observed in the region 2800-3200 cm⁻¹. Accordingly, in the present study for 2, 5-Dimethoxybenzonitrile, the C-H stretching vibrations are calculated at 2888, 2894, 2943, 2951, 3020 and 3027 cm⁻¹, respectively.

Spectral region from 1000 cm⁻¹ to 2300 cm⁻¹:

The C-H and C-C wagging vibrations are observed at 1210, 1249, 1259, 1397 cm⁻¹. In plane bending vibrations are found at 1447 cm⁻¹ and 1477 cm⁻¹. Between the region 1000- 2300 cm⁻¹, we have observed intense peak at 1010 cm⁻¹ and 1296 cm⁻¹ due to the whole ring deformed. Also C-N stretching vibration is calculated in 2254 cm⁻¹ region.

Spectral region below 1000 cm⁻¹:

Out of plane banding in C-H observed at 792 and 867 cm⁻¹. Ring Breathing vibrations are observed at 691 cm⁻¹ and 739 cm⁻¹ while Twisting in C-N bond is shown in 491 cm⁻¹. Ring Torsion modes are shown at 278 cm⁻¹ in the calculated spectra.

Conclusion

We have done a Structural, electronic, optical and vibrational properties of 2, 5 Dimethoxybenzonitrile Using Density Functional Theory. All frequencies are real in the molecule. Hence the compound is stable. The method B3LYP /6-311G (d, p) gives us most successfully described the vibrational spectra of 2, 5-Dimethoxybenzonitrile. Reactivity reflects the susceptibility of a substance towards a specific chemical reaction and plays a key role in, for example, the design of new molecules and understanding biological systems and material science. Hyper polarizability is mainly controlled by the planarity of the molecules, the donor and acceptor strength, and bond length alteration. The values of hyper polarizability indicate a possible use of these compounds in electro-optical applications. The present work might encourage the need for an extensive study by the experimentalists interested in the vibrational spectra and the structure of these compounds.

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Notes and References

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