



**COMPUTATIONAL STUDY ON MOLECULAR STRUCTURE, VIBRATIONAL SPECTROSCOPIC STUDIES AND ANALYSIS OF 2-METHOXYBENZONITRILE**

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**ABSTRACT**

Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of ab initio Hartree-Fock (HF) and density functional theory (DFT) gradient calculations with complete relaxation in the potential energy surface using 6-311++G(d,p) basis set. The calculated HOMO-LUMO energy gap reveals that charge transfer occurs within the molecule. Stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using natural bond orbitals (NBO) analysis. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution (TED).

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**INTRODUCTION**

The many organic molecules studied for future applications through the experimental as well as the theoretical methods in the various twigs of the science and engineering [1]. The theoretical methods have the fast and furious results for the larger molecules to evaluate the applications in addition to their physicochemical properties. The computational techniques powerful tool for the pin pointed answers for the molecules, So as to corroborate and yet expand the experimental results. It is a vast and versatile component in the chemicals, which is called cyanobenzene or phenyl cyanide. The special benzonitrile derivatives like organic acids (benzoic acid, mandelic acid), amines (benzyl amine, pyridine), neutrals (benzonitrile, toluene) and benzonitrile herbicides. Benzonitrile is an applicable as solvent and precursor to number of derivatives. One of the benzonitrile derivatives is used in Pharmaceutical and Agrochemical Intermediates, Epoxy curing agent. Moreover Benzonitrile is mainly used for the agriculture fields, which households to control the growth of weeds and their residues persist in the reported literature [2].

Recently, Benzonitrile is used as most excellent solvent and versatile precursor chemical intermediate in many derivatives.

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Benzonitrile compounds are the origin of many compounds like benzoguanamine, pesticides, intermediates of aliphatic amine and benzoic acid [3-4]. Dye-Sensitized Solar Cells (DSSCs) are recently the most efficient and low-cost third-generation solar technology, which is the trendiest tremendous interest as a green and renewable energy conversion device [5-7]. In the DSSC, the dye sensitizers are act as a superior and crucial part in the future researches [8]. The properties of the dye sensitizers like physical, electronic, thermal are required for the DSSC synthesis. So the theoretical and computational investigations of these dyes sensitizers have become essential phenomena, to identify the innovative dye sensitizers with the enhancing properties.

To the best of our knowledge, the vibrational assignments and other properties never determined for this compound still now. So this article going to serve about complete vibrational assignments of different modes of molecules. And electronic and thermo studies are simultaneously take over to the molecule. In this paper the performance of 2-methoxybenzonitrile metal free dye that can be used in DSSC is analyzed theoretically. Electronic absorption spectra and sensitized mechanism are determined using gaseous state and solvent as Acetonitrile. The author had drawn the isodensity plots of frontier molecular spectra. The role of nitro group in 2-methoxybenzonitrile in geometries, electronic structures, and spectral properties analyzed [9-11].

## Computational Details

To provide complete information regarding the structural characteristics and the fundamental vibrational modes of DMAP, the Restricted Hartree–Fock and DFT-B3LYP correlation functional calculations [12-13] have been carried out. The calculations of geometrical parameters in the ground state were performed using Gaussian 09 programs [14], invoking gradient geometry optimization [15] on Intel core i3/2.93 GHz processor. The computations were performed at HF/6-311++G(2d,p) and B3LYP/6-311++G(2d,p) levels to obtain the optimized geometrical parameters, vibrational wave numbers of the normal modes, IR intensity, Raman intensity, UV-vis absorbance, NLO, NPA, atomic charges and thermodynamical parameters of the compound. DFT calculations were performed using Becke's three-parameter hybrid model using Lee–Yang–Parr (B3LYP) correlation function method. Some Spectrums were drawn using Gaussian Sum.

## RESULTS AND DISCUSSION

### The geometric structure

It belongs to the C1 point group symmetry. Fig. 1 shows the optimized geometry of the molecule and Table 1 presents the optimized values obtained for bond lengths and bond angles. The equilibrium geometrical parameters namely atomic lengths, atomic angles and dihedral angles calculated by dissimilar levels are listed. The predicted geometrical optimized molecular structure of 2-methoxybenzonitrile has 17 atoms among 45 symmetry species of vibrations that are obtained chemcraft program is shown in Fig.1. The optimized bond lengths of C3-C4 and C8-C9 is 1.395 and 1.429 Å respectively at B3LYP/6-311G (2d, p) and also well matched with HF/6-311G (2d, p).

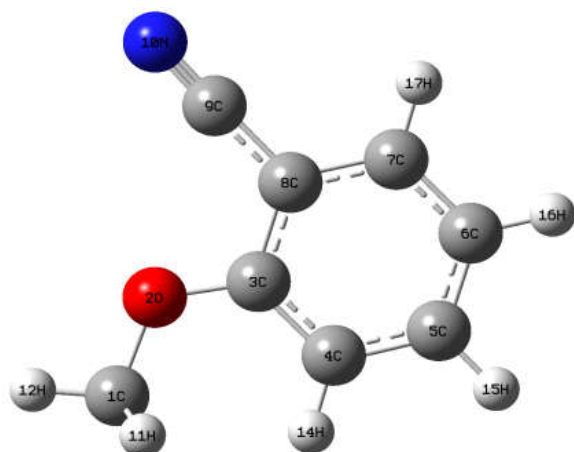


Figure 1 Optimized Structure

The various bond lengths and bond angles are found to be almost same at all basis sets. The carbon to carbon atoms bond length has same values. The bond length between O2–C3 in HF and B3LYP are 1.30 and 1.35 respectively. The bond angle between carbons angles are almost same for the all basis sets. The bond angle between O2–C3–C4 in HF, B3LYP basis sets values are 120 and 125 respectively. The dihedral angle between C8–C9–N10–H11 in HF, B3LYP method values are 180. The calculated geometric parameters can be used to determine the other parameters of 2-methoxybenzonitrile. All basis set values are almost well agreement with microwave data [16].

Table 1 Give the optimized values obtained for bond lengths and bond angles

Bond Length (Å)	Bond Angle (°)			Dihedral Angle (°)					
	A	B	C	A	B	A	B		
C1-O2	1.42	1.43	1.39	O2-C1-H11	111	109	H11-C1-O2-C3	61	90
C1-H11	1.09	1.07	0.98	O2-C1-H12	106	109	H12-C1-O2-C3	-180	-150
C1-H12	1.09	1.07	0.95	O2-C1-H13	111	109	H13-C1-O2-C3	-61	-30
C1-H13	1.09	1.07	0.95	H11-C1-H12	110	109	C1-O2-C3-C4	0	0
O2-C3	1.35	1.30	1.44	H11-C1-H13	110	109	C1-O2-C3-C8	-180	180
C3-C4	1.39	1.40	1.39	H12-C1-H13	110	109	O2-C3-C4-C5	-180	180
C3-C8	1.41	1.40	1.39	C1-O2-C3	119	120	O2-C3-C4-H14	0	0
C4-C5	1.39	1.40	1.40	O2-C3-C4	125	120	C8-C3-C4-C5	0	0
C4-H14	1.08	1.07	0.95	O2-C3-C8	116	120	C8-C3-C4-H14	-180	180
C5-C6	1.39	1.36	1.39	C4-C3-C8	119	119	O2-C3-C8-C7	180	180
C5-H15	1.08	1.07	0.95	C3-C4-C5	120	120	O2-C3-C8-C9	0	0
C6-C7	1.39	1.36	1.40	C3-C4-H14	120	120	C4-C3-C8-C7	0	0
C6-H16	1.08	1.07	0.95	C5-C4-H14	120	120	C4-C3-C8-C9	180	180
C7-C8	1.40	1.40	1.44	C4-C5-C6	121	120	C3-C4-C5-C6	0	0
C7-H17	1.08	1.07	0.95	C4-C5-H15	119	120	C3-C4-C5-H15	-180	180
C8-C9	1.43	1.40	1.40	C6-C5-H15	120	120	H14-C4-C5-C6	180	180
C9-N10	1.15	1.15	1.14	C5-C6-C7	119	121	H14-C4-C5-H15	0	0
				C5-C6-H16	121	120	C4-C5-C6-C7	0	0
				C7-C6-H16	120	120	C4-C5-C6-H16	180	180
				C6-C7-C8	121	120	H15-C5-C6-C7	180	180
				C6-C7-H17	121	120	H15-C5-C6-H16	0	0
				C8-C7-H17	119	120	C5-C6-C7-C8	0	0
				C3-C8-C7	120	120	C5-C6-C7-H17	-180	180
				C3-C8-C9	120	120	H16-C6-C7-C8	-180	180
				C7-C8-C9	120	120	H16-C6-C7-H17	0	0
							C6-C7-C8-C3	0	0
							C6-C7-C6-C9	-180	180
							H17-C7-C8-C3	180	180
							H17-C7-C8-C9	0	0
							C8-C9-N10-H11-1	182	180
							C8-C9-N10-H11	180	180

A- B3LYP/6-311++G(2d,p); B- HF/6-311++G(2d,p); C- Microwave Data(benzonitrile).

### Electronic structures UV-Vis and charges

Natural Bond Orbital (NBO) analysis was performed in order to analyze the charge populations of the dye 2-methoxybenzonitrile. Charge distributions in C, N and H atoms were observed because of the different electronegativity, the electrons transferred from C atoms to C, N atoms, C atoms to H [17]. The natural charges of different groups are the sum of every atomic natural charge in the group. These data indicate that the cyanine and amide groups are acceptors, while the acetic groups are donors, and the charges were transferred through chemical bonds. The frontier molecular orbitals (MO) energies of the dye 2-methoxybenzonitrile is shown in Fig. 2. The HOMO–LUMO gap of the dye 2-methoxybenzonitrile in vacuum is 5.26 eV and equal wavelength is 265nm which is used as a potential source for UV light in Fig.3.

The calculated MPA and NPA atomic charges of 2-methoxybenzonitrile are compared in Table 2. The two methods predict the equivalent propensities. The both atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of dipole moment, polarizability, atomic charge effect, electronic structure and a lot of properties of molecular systems.

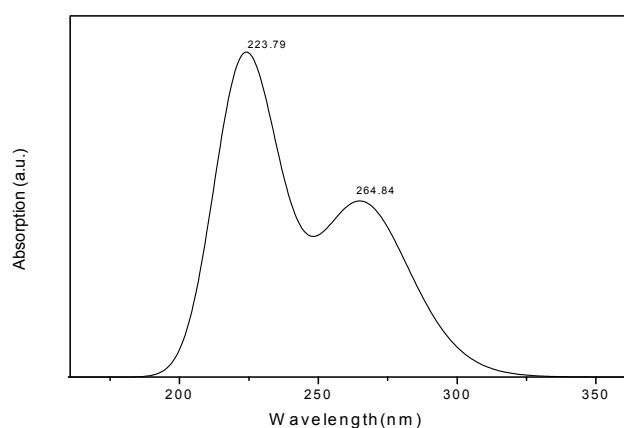


Figure 3 UV-Vis spectrums

**Table 2** Comparison of calculated energies, excitation energies, oscillator strengths, dipole moments and frontier orbital energies for the different compound

Basic set	A	B
SCF energy(a.u)	-439.1307414	-436.4241264
Dipole moment(Debye)	2.2944	2.35
LUMO(eV)	-1.8	0.81
HOMO(eV)	-7.06	-9.13
ENERGY GAP(eV)	-5.26	-9.94
Electronegativity ( $\chi$ )	-4.43	-4.16
Chemical Potential ( $\mu$ )	4.43	4.16
Global Hardness ( $\eta$ )	2.63	4.97
Global softness (s)	0.380228137	0.201207243
Electrophilicity Index ( $\omega$ )	5.82545	10.3376
EHOMO-1(eV)	-7.65	-9.89
ELUMO+1(eV)	-1.05	1.09
EHOMO-1 - ELUMO+1(eV)	-6.6	-10.98

### Charge analysis

The charges are computed by MA with same basic sets tabulated in Table 3. MA graph of 2-methoxybenzonitrile molecule has been drawn in the Fig.4. MA charges are the main impact for the functions like as quantum mechanical calculations, electronic effects, polarizability changes, Dipole moments and other properties of the molecules. The polarization changes decided the charges by the different basis sets [18].

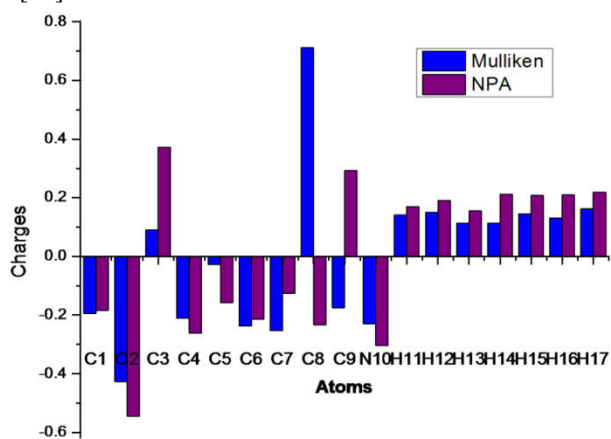


Figure 4 Mulliken Charge comparison for 2-methoxybenzonitrile

In this research molecule, Carbon atom has both sign values in two methods. The positive charge distribution of Hydrogen atoms are acts as an acceptors, and the opposite trends of the atoms Nitrogen, Bromine are acts as a donor. Conclude from the overall comparison, (2d,p) basis sets atoms charge distribution values are higher than (d,p).

**Table 3** Mulliken Charges for 2-methoxybenzonitrile

S.NO	Atoms	Mulliken	NPA
		6-311++G(2d,p)	
1	C1	-0.194386	-0.18379
2	O2	-0.426984	-0.54551
3	C3	0.089257	0.37289
4	C4	-0.211434	-0.26173
5	C5	-0.027924	-0.15819
6	C6	-0.237683	-0.21421
7	C7	-0.253401	-0.12573
8	C8	0.711299	-0.23346
9	C9	-0.174991	0.29176
10	N10	-0.229149	-0.30331
11	H11	0.140423	0.16974
12	H12	0.150931	0.19007
13	H13	0.112651	0.15486
14	H14	0.112701	0.21165
15	H15	0.144936	0.20709
16	H16	0.131258	0.20964
17	H17	0.162497	0.21823

### First hyperpolarizability

The hyperpolarizability is contributed by the structure, bonding and vibrational of the molecule. The dipole moment and hyperpolarizability of the benzonitrile is high. In the recent molecule has been calculated the enhanced hyperpolarizability value which is due to the substituent of the benzonitrile. The bond and vibrational results are confirmed the envelope to the hyperpolarizability enlargement of the 2-methoxybenzonitrile molecule. The dipole moment ( $\mu$ ), polarizability ( $\alpha$ ), anisotropy polarizability ( $\alpha_0$ ) and hyperpolarizability ( $\beta_0$ ) of the title molecule have calculated by the B3LYP/6-311++G (2d, p) methods based on the finite-field approach and the values are tabulated in the Table 3. The electric is the task for the energy of the scheme because an electrical meadow exists in the molecule. The  $\beta_0$  is a third-rank tensor that is able to be portrayed by a  $3 \times 3 \times 3$  matrix. The Kleinman symmetry diminished the 27 mechanisms into 10 mechanisms [19]. The mechanisms of distinct as the constants in the Taylor series of energy in an external electric meadow. When an external electric meadow is feeble and harmonized, the above series becomes

$$E = E^0 - \frac{\mu_i}{1!} - \frac{\alpha_{ij}F_iF_j}{2!} - \frac{\beta_{ijk}F_iF_jF_k}{3!} - \frac{\gamma_{ijkl}F_iF_jF_kF_l}{4!} + \dots (1)$$

In the title molecule dipole moment is 2.2944Debye, polarizability is  $2042.948 \times 10^{-33}$ esu, and hyperpolarizability is  $2280.4468 \times 10^{-30}$ esu, calculated. The over parameters values are the mainly reason for the NLO property using below equations.

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

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{1/2} \quad (4)$$

$$\beta_0 = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{zzy} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2} \quad (5)$$

The calculated hyperpolarizability values are 9.61 times better than that of urea ( $\beta_0$  of urea  $0.3728 \times 10^{-30}$ esu with the same method). So this 2-methoxybenzotrile is good optical property crystal with high polarizability values and helpful for further optical responses.

**Table 4** NLO parameters for 2-methoxybenzotrile

Parameters	B3LYP/6-311++G(2d,p)	Parameters	B3LYP/6-311++G(2d,p)
$\mu_x$	1.5013824	$\beta_{xxx}$	177.7238969
$\mu_y$	0.7831196	$\beta_{xxy}$	-21.1186616
$\mu_z$	-1.5482252	$\beta_{xyy}$	50.5842773
$\mu=$	2.2944Debye	$\beta_{yyy}$	41.11086
$\alpha_{xx}$	124.5176941	$\beta_{xxz}$	58.3428476
$\alpha_{xy}$	16.1495015	$\beta_{xyz}$	37.3628126
$\alpha_{yy}$	75.4220753	$\beta_{yyz}$	-9.19458
$\alpha_{xz}$	-1.1237332	$\beta_{xzz}$	31.97993
$\alpha_{yz}$	-23.604	$\beta_{yzz}$	-23.7512737
$\alpha_{zz}$	109.5952844	$\beta_{zzz}$	-5.4229116
$\alpha_0$	$236.4715 \times 10^{-33}$ esu	$\beta_0$	$2280.4468 \times 10^{-33}$ esu
$\alpha=$	$2042.948 \times 10^{-33}$ esu		

## CONCLUSION

The geometries, electronic structures, polarizabilities, and hyperpolarizabilities of dye 2-methoxybenzotrile was studied by using ab initio HF and density functional theory with hybrid functional B3LYP, and the UV-Vis spectra were investigated by using TD-DFT methods. The NBO results suggest that 2-methoxybenzotrile is a (D-p-A) system. The calculated isotropic polarizability of 2-methoxybenzotrile is  $236.4715 \times 10^{-33}$ esu. The calculated polarizability anisotropy invariant of 2-methoxybenzotrile is  $2042.948 \times 10^{-33}$ esu. The hyperpolarizability of 2-methoxybenzotrile is  $2280.4468 \times 10^{-33}$ esu. This indicates that the choice of the appropriate conjugate bridge in dye sensitizer is very important to improve the performance of DSSC.

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