

Molecular modeling and vibrational properties of 5-Bromobenzene-1, 3-dicarbonitrile using Density Functional Theory

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Nitriles are found in many useful compounds, including methyl cyanoacrylate, used in super glue, and nitrile butadiene rubber. So we have done a vibrational spectroscopic investigation on 5-Bromobenzene-1, 3-dicarbonitrile which has a nitrile group. The optimized geometry of the 5-Bromobenzene-1, 3-dicarbonitrile 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 5-Bromobenzene-1, 3-dicarbonitrile. A complete assignment is provided for the observed FTIR spectra.

Introduction

A nitrile is any organic compound that has a $-C\equiv N$ functional group. The prefix cyano- is used interchangeably with the term nitrile in industrial literature. Nitriles are found in many useful compounds, including methyl cyanoacrylate, used in super glue, and nitrile butadiene rubber, a nitrile-containing polymer used in latex-free laboratory and medical gloves. Organic compounds containing multiple nitrile groups are known as cyanocarbons. Inorganic compounds containing the $-C\equiv N$ group are not called nitriles, but cyanides instead. Though both nitriles and cyanides can be derived from cyanide salts, most nitriles are not nearly as toxic. The N-C-C skeleton is linear in nitriles, reflecting the sp hybridization of the triply bonded carbon. The C-N distance is short at 1.16 Å, consistent with a triple bond. Nitriles are polar, as indicated by high dipole moments. Nitrile groups in organic compounds can undergo various reactions when subject to certain reactants or conditions. A nitrile group can be hydrolyzed, reduced, or ejected from a molecule as a cyanide ion. In many instances the nitrile mimics functionality present in substrates for enzymes, whereas in other cases the nitrile increases water solubility or decreases susceptibility to oxidative metabolism in the liver. The nitrile functional group is found in several drugs [1, 2]. As a part of our ongoing research work [3-10], we report the comparative study of 5-Bromobenzene-1, 3-dicarbonitrile by DFT study. To the best of our knowledge no comparative quantum chemical calculations of these molecules have been reported so far in the literature.

Computational details

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) [11] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [12] has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, and energies of the optimized structures, using GAUSSIAN 09 [13]. The calculated vibrational frequencies have also been scaled by a factor of 0.963 [14]. By combining the results of GaussView's program [15] 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 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 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

The optimized Structure parameters of 5-Bromobenzene-1, 3-dicarbonitrile 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, respectively. After geometry optimization local minimum energy obtained for structured optimization of 5-Bromobenzene-1, 3-dicarbonitrile with 6-311G (d, p) basis set is approximately -2990.3711 (a.u.). For B3LYP method, the optimized bond parameters of molecule calculated by various methods are listed in Table 1.

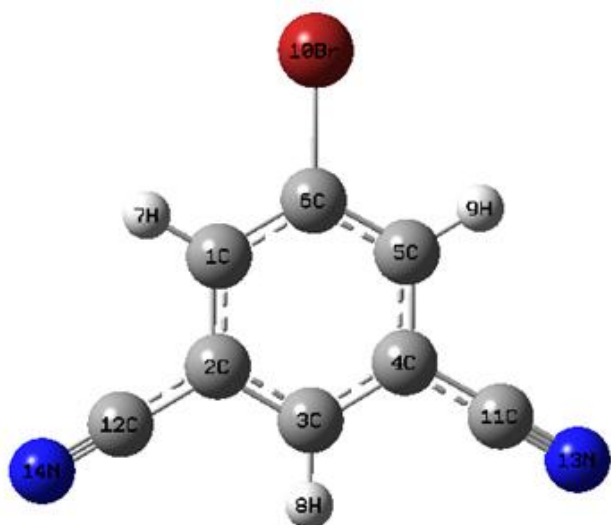


Figure 1 Model molecular structure of 5-Bromobenzene-1, 3-dicarbonitrile

Table 1 Bond Length (Å) and Bond Angle of 5-Bromobenzene-1, 3-dicarbonitrile

Parameter	Experimental value	Calculated value
C ₁ -C ₂	1.398	1.402
C ₁ -C ₆	1.305	1.389
C ₁ -H ₇	0.950	1.081
C ₂ -C ₃	1.386	1.397
C ₂ -C ₁₂	1.449	1.431
C ₃ -C ₄	1.393	1.397
C ₃ -H ₈	0.950	1.081
C ₄ -C ₅	1.396	1.402
C ₄ -C ₁₁	1.447	1.431
C ₅ -C ₆	1.386	1.389
C ₅ -H ₉	0.950	1.081
C ₆ -Br ₁₀	1.888	1.907
C ₁ -N ₁₃	1.143	1.154
C ₁₂ -N ₁₄	1.134	1.154
C ₂ -C ₁ -C ₆	118.3	119.1
C ₂ -C ₁ -H ₇	120.8	120.0
C ₆ -C ₁ -H ₇	120.8	120.7
C ₁ -C ₂ -C ₃	121.7	120.5
C ₁ -C ₂ -C ₁₂	118.8	119.5
C ₃ -C ₂ -C ₁₂	119.3	119.8
C ₂ -C ₃ -C ₄	118.3	119.2
C ₂ -C ₃ -H ₈	120.8	120.3
C ₄ -C ₃ -H ₈	120.8	120.3
C ₃ -C ₄ -C ₅	121.3	120.5
C ₃ -C ₄ -C ₁₁	118.9	119.8
C ₅ -C ₄ -C ₁₁	119.8	119.5
C ₄ -C ₅ -C ₆	118.6	119.1
C ₄ -C ₅ -H ₉	120.7	120.0
C ₆ -C ₅ -H ₉	120.7	120.7
C ₂ -C ₆ -C ₅	121.6	121.3
C ₁ -C ₆ -Br ₁₀	119.1	119.3
C ₅ -C ₆ -Br ₁₀	119.2	119.3
C ₄ -C ₁₁ -N ₁₃	178.8	179.9
C ₂ -C ₁₂ -N ₁₄	179.7	179.9

The (C-C) bond length varies between 1.389Å- 1.431Å, while (C-H) bond length is constant i.e. 1.081Å. (C-Br) bond length is 1.907Å, while (C-N) bond length is constant i.e. 1.14Å. The (C-C-C) bond angle varies between 119.1- 121.3, while (C-C-H) bond angle varies between 120.0- 120.7. The (C-C-Br) bond angle is 119.3, while for (C-C-N), bond angle is 179.9. All the calculated bond angles are in good agreement with experimental data as given in Table 1.

Table 2 Mulliken Atomic Charges of 5-Bromobenzene-1, 3-dicarbonitrile

S.No.	Atoms	Atomic charges
1.	C	0.064017
2.	C	-0.048967
3.	C	0.045847
4.	C	-0.048934
5.	C	0.064024
6.	C	-0.209894
7.	H	0.139523
8.	H	0.136501
9.	H	0.139523
10.	Br	0.031776
11.	C	0.039639
12.	C	0.039669
13.	N	-0.196373
14.	N	-0.196351

Atomic charge, Polarizability, Hyper Polarizability and Thermodynamic Properties:

The Mulliken atomic charges for all the atoms of the 5-Bromobenzene-1, 3-dicarbonitrile 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 [16, 17] 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. = 8.3693X10⁻³³ e.s.u.). For 5-Bromobenzene-1, 3-dicarbonitrile, the calculated dipole moment value is 2.9083 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 Z direction. β_{xxx} , β_{xyy} contribute larger part of hyperpolarizability in the molecule. This shows that X-axis and XY

plane more optical active in these direction.

Table 3 Polarizability and Hyper Polarizability of 5-Bromobenzene-1, 3-dicarbonitrile

Polarizability	
α_{xx}	-82.1526
α_{xy}	-0.0013
α_{yy}	-96.7513
α_{yz}	0.0002
α_{zz}	-75.5979
α_{zx}	-0.0102
α	85.8339
Hyper Polarizability	
β_{xxx}	123.3954
β_{xxy}	0.0079
β_{xyy}	118.6658
β_{yyy}	-0.0126
β_{yzz}	-0.0004
β_{xzz}	-0.0012
β_{xzz}	28.6983
β_{vzz}	0.0002
β_{vyz}	0.0002
β_{xvz}	0.0094
β	270.7595

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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 thermodynamical behavior of title compounds.

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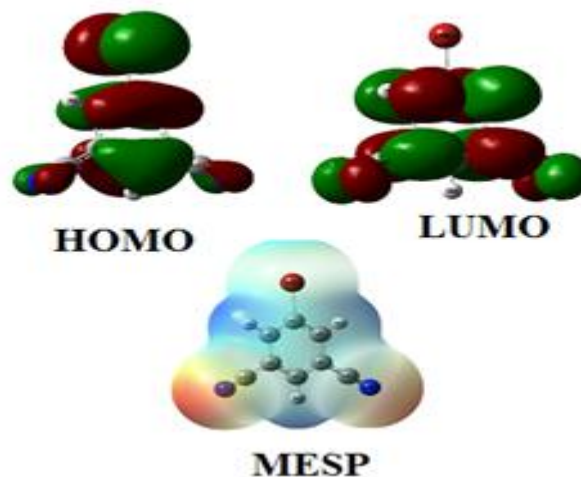
Table 4 Thermodynamic Properties of 5-Bromobenzene-1, 3-dicarbonitrile

Parameter	E (Thermal) kcal/Mol	C_v cal/mol- Kelvin	S cal/mol- Kelvin
Total	60.537	33.593	98.035
Translational	0.889	2.981	41.872
Rotational	0.889	2.981	31.966
Vibrational	58.760	27.631	24.198

20 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 [18]. The frontier orbital gap in case of the given molecule is 3.726 eV for 5-Bromobenzene-1, 3-dicarbonitrile given in Table 5.

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Figure 2 HOMO - LUMO and MESP pictures of 5-Bromobenzene-1, 3-dicarbonitrile

The contour plots of the HOMO, LUMO structure and MESP diagram of the molecule is 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 [19, 20].

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Table 5 Total energy, Dipole Moment, HOMO, LUMO and Energy gap of 5-bromobenzene-1, 3- dicarbonitrile

Parameters	Value
Total Energy E (a.u.)	-2990.3711
Dipole moment (Debye)	2.9083
LUMO (a.u.)	-0.14464
HOMO (a.u.)	-0.28166
Frontier orbital Energy Gap (eV)	3.726944

45 Assignment of fundamentals

5-Bromobenzene-1, 3-dicarbonitrile has 14 atoms with 36 normal modes of vibration. We made reliable one to one correspondence between the fundamentals and the frequencies calculated by DFT (B3LYP) methods. The relative band intensities are also very satisfactory along with their position. Some important modes are discussed hereafter in table 6 for 5-Bromobenzene-1, 3-dicarbonitrile.

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Vibrational modes description

Spectral region above 2800 cm^{-1}

C-H stretching vibrations are generally observed in the region 2800-3200 cm^{-1} . Accordingly, in the present study for 5-Bromobenzene-1, 3-dicarbonitrile, the C-H stretching vibrations are presented at 3095, 3096, 3097 cm^{-1} in calculated spectrum.

Spectral region from 1000 to 2300 cm^{-1}

Butterfly motion vibration is observed at 1091 cm^{-1} , while Ring Breathing vibration in molecule is observed at 1221 cm^{-1} . C-H wagging are observed at 1281 and 1391 cm^{-1} and also Ring Deformation modes in molecule are observed at 1398, 1535 and

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1569 cm⁻¹ in calculated spectrum.

Spectral region below 1000 cm⁻¹

Out of plane banding in C-N are calculated at 95 and 667 cm⁻¹, while out of plane banding in C-H is calculated at 870 cm⁻¹.

5 Again interesting butterfly motion is found at 108 cm⁻¹ and whole ring torsion mode is observed at 786 cm⁻¹ in calculated spectrum.

Table 6 Calculated Wave Numbers and its respective I.R. Intensity of 5-Bromobenzene-1,3-dicarbonitrile

S.No.	Frequency	IR intensity	Vibrational assignments ^a
1.	95	7.678	Out of plane Banding(C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
2.	108	6.504	Butterfly Motion
3.	119	1.602	Twisting(C ₂ -C ₁₂ -N ₁₄)+(C ₄ -C ₁₁ -N ₁₃)
4.	157	0	Twist in (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
5.	170	1.225	Twist in (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
6.	262	1.216	τ(C ₃ -C ₄ -C ₁₁ -N ₁₃)+(C ₁ -C ₂ -C ₁₂ -N ₁₄)
7.	290	4.200	Stretching in whole ring
8.	367	0	τ (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
9.	413	8.108	τ (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
10.	445	0.020	Ring Torsion
11.	447	0.068	τ (C ₃ -C ₄ -C ₁₁ -N ₁₃)+(C ₁ -C ₂ -C ₁₂ -N ₁₄)
12.	517	0.701	τ (C ₅ -C ₄ -C ₁₁ -N ₁₃)+(C ₃ -C ₂ -C ₁₂ -N ₁₄)
13.	553	0.156	Twist in (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
14.	606	0.026	τ (C ₁ -C ₂ -C ₁₂ -N ₁₄)+(C ₃ -C ₄ -C ₁₁ -N ₁₃)
15.	622	0	Out of plane(τ)(C ₁ -C ₂ -C ₁₂ -N ₁₄)+(C ₅ -C ₄ -C ₁₁ -N ₁₃)
16.	667	22.17	Out of plane(Twist)(C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
17.	786	51.88	Torsion in whole ring
18.	870	27.70	Out of plane banding(H ₇ -C ₁)+(C ₅ -H ₉)
19.	895	5.985	Out of plane banding(C ₃ -H ₈),Twist(C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
20.	896	0	Twisting (C ₁₂ -N ₁₄)+(C ₁₁ -N ₁₃)
21.	907	4.047	Breathing
22.	972	0.854	Breathing
23.	1091	11.22	Butterfly Motion
24.	1127	1.672	Torsion (H ₉ -C ₅ -C ₄ -C ₁₁)+(H ₈ -C ₃ -C ₂ -C ₁₂)
25.	1221	22.35	Breathing
26.	1235	1.370	Ring twist
27.	1281	0.085	Wagging(ω)(C ₃ -H ₈)+(C ₁ -H ₇)
28.	1391	12.93	Wagging(ω)(C ₁ -H ₇)+(C ₃ -H ₈)
29.	1398	11.20	Ring deformation
30.	1535	65.52	Ring deformation
31.	1569	4.726	Ring deformation
32.	2260	14.07	v (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
33.	2262	5.872	v (C ₁₁ -N ₁₃)+(C ₁₂ -N ₁₄)
34.	3095	2.724	v (C ₁ -H ₇)+(C ₅ -H ₉)
35.	3096	1.622	v (C ₁ -H ₇)+(C ₅ -H ₉)
36.	3097	0.971	v (C ₃ -H ₈)

^afor atomic labelling, please refer to Figure 1.

Conclusions

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.

15 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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