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MOLECULAR STRUCTURE, ELECTRONIC PROPERTIES AND VIBRATIONAL ANALYSIS OF 5-BROMOBENZENE 1, 3-DI CARBONITRILE

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ABSTRACT

The aromatic nitriles, being used as pharmaceuticals, liquid crystals, dyes and synthetic intermediates for agrochemicals and functional materials have been under investigation for a long time. In a recent study, scientists synthesized and studied the crystal structure of 5-Bromobenzene 1, 3-dicarbonitrile. Keeping various applications of aromatic nitriles in mind, quantum chemical calculations of energies, geometrical structure and vibrational wave numbers were carried out by DFT methods with 6-311++G(d,p) basis sets. A study on the electronic, dipole moment and frontier molecular orbital energies were also performed. HOMO and LUMO energy gap confirm the occurring of charge transformation in the molecule. The Frontier Molecular Orbital's (FMO), Molecular Electrostatic Potential were studied. The theoretical IR spectra for the title compound has been also calculated. Molecular electrostatic potential surfaces have also been calculated to explore the reactive sites of the molecule under consideration.

Keywords: Aromatic nitriles, Vibrational Analysis, Frontier Molecular Orbital.

1. INTRODUCTION

Diversely utilised aromatic nitriles have used in organic synthesis, also in crystal engineering and in the construction of metal organic frameworks [1, 2]. They can be easily transformed into esters, amides, carboxylic acids, amines, amidines, ketones and nitrogen containing heterocycles such as tetrazoles, oxazoles and natural products [3]. Moreover, aromatic nitriles are used as pharmaceuticals, liquid crystals, dyes and synthetic intermediates for agrochemicals, pharmaceuticals, and functional materials [4]. For example, Periciazine (anti-psychotic drug), Fadrozole (oncolytic drug), Letrozole (breast cancer therapy), Etravirine (anti-HIV) are some pharmaceutically important aromatic nitriles [5]. Recently X-ray crystal structure data of 5-bromobenzene 1, 3-di carbonitrile (BBDCN) have been reported by Seidel et al. [6]. Keeping above in mind, we are presenting here the results from DFT/B3LYP calculations of the molecular structure, electronic properties and vibrational spectra of 5-bromobenzene 1, 3-di carbonitrile (BBDCN) molecule. This study on BBDCN molecule, comprised of equilibrium geometries optimization and the calculation of molecular ground state properties at DFT/6-311++G (d, p) level of theory. Theoretical IR spectra and normal mode analysis of title compound has also been calculated. The vibrational analysis yields the detailed information about the intermolecular vibrations of the title molecule. The structure activity relationship based on the study of frontier orbital gap, dipole moment data along with the molecular electrostatic potential map of the BBDCN molecule has been used to understand the active sites of the molecule.

2. MATERIAL AND METHODS

The title molecule BBDCN was analysed with Density Functional theory [7] employing Becke's 3-parameter hybrid exchange functional [8] with Lee Yang Parr functional (LYP) [9, 10] and 6-311++G (d, p) basis set using the Gaussian 09 program package [11]. By combining the results of Gauss View program package [12] and VEDA 4 program [13] vibrational frequency assignments have been calculated with a high degree of accuracy. Molecular electrostatic potential surface (MEPS) has been computed at the same level of theory and plotted using Gauss View 5.

3. RESULTS AND DISCUSSION

3.1. Molecular geometry

The geometry optimization is one of the important steps in the quantum chemical calculation. This is achieved by energy minimization using DFT at the B3LYP level, employing the split valence basis set 6-311++G (d, p). The optimized geometry of molecule (Fig.1.) under study is confirmed to be located at the local true minima on potential energy surface, as the calculated vibrational spectra contains no imaginary wavenumbers.

The optimized structural parameters (bond lengths, bond angles, dihedral angles) of BBDCN have been compared with the earlier reported experimental crystal structure data [6] as shown in Table 1. The whole molecule is nearly planer as evident from dihedral angles data as these are either zero degree or 180 degree.

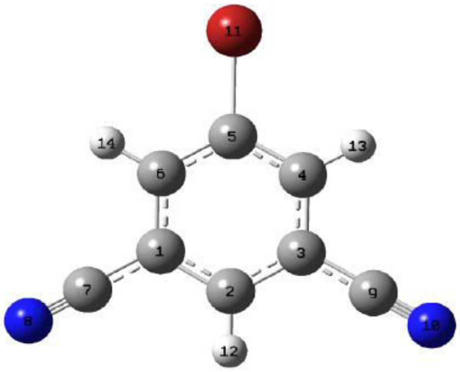

Fig. 1: The optimised structure of BBDCN molecule

Table 1: Comparison of optimized parameters of BBDCN at B3LYP/6-311++G (d,p) with experimental data

S.N.	Parameter	Theoretical Value	Experimental Value[6]
		Bond Length (Å)	
1	C1-C2	1.3979	1.3973
2	C1-C6	1.4027	1.3953
3	C1-C7	1.4322	1.4493
4	C2-C3	1.3979	1.3933
5	C2-H12	1.0819	0.9500
6	C3-C4	1.4027	1.3973
7	C3-C9	1.4322	1.4473
8	C4-C5	1.3899	1.3793
9	C4-H13	1.0817	0.9500
10	C5-C6	1.3899	1.3953
11	C5-Br	1.9076	1.8862
12	C6-H14	1.0817	0.9500
13	C7-N8	1.1547	1.1393
14	C9-N10	1.1547	1.1413
		Bond Angle	
1	C2-C1-C6	120.5938	121.7119
2	C2-C1-C7	119.8626	120.9018
3	C6-C1-C7	119.5435	117.3918
4	C1-C2-C3	119.2704	118.0519
5	C1-C2-H12	120.3648	121.0
6	C3-C2-H12	120.3649	121.0
7	C2-C3-C4	120.594	121.2219
8	C2-C3-C9	119.8626	120.22
9	C4-C3-C9	119.5434	118.62
10	C3-C4-C5	119.0944	119.12
11	C3-C4-H13	120.0657	120.5
12	C5-C4-H13	120.84	120.5
13	C4-C5-C6	121.353	121.6019
14	C4-C5-Br	119.3235	120.2316
15	C6-C5-Br	119.3235	118.1815
16	C1-C6-C5	119.0945	118.3619
17	C1-C6-H14	120.0656	120.8
18	C5-C6-H14	120.8399	120.8

		Dihedral Angle	
1	C6-C1-C2-C3	0.0001	0.73
2	C6-C1-C2-H12	179.9992	-
3	C7-C1-C2-C3	179.9994	-178.8719
4	C7-C1-C2-H12	-0.0015	
5	C2-C1-C6-C5	-0.0002	-0.33
6	C2-C1-C6-H14	-180.0002	-
7	C7-C1-C6-C5	180.0005	179.2919
8	C7-C1-C6-H14	0.0005	-
9	C1-C2-C3-C4	-0.0001	-0.53
10	C1-C2-C3-C9	179.9994	179.22
11	H12-C2-C3-C4	-179.9992	-
12	H12-C2-C3-C9	0.0015	-
13	C2-C3-C4-C5	0.0003	-0.23
14	C2-C3-C4-H13	180.0002	-
15	C9-C3-C4-C5	-180.0004	-179.92
16	C9-C3-C4-H13	-0.0005	-
17	C3-C4-C5-C6	-0.0004	-0.73
18	C3-C4-C5-Br	179.9991	179.3516
19	H13-C4-C5-C6	179.9996	-
20	H13-C4-C5-Br	-0.0009	-
21	C4-C5-C6-C1	0.0004	0.43
22	C4-C5-C6-H14	-179.9996	-
23	Br-C5-C6-C1	179.9991	179.6215
24	Br-C5-C6-H14	0.0009	-

In comparison with the experimental values, it can be observed that most of the bond length values are slightly larger than the experimental values, while some of them are lesser also such as the bond lengths of C1-C7, C3-C9, and C5-C6. This may be due to the fact that the calculations performed were for an isolated molecule (gaseous phase) whereas in experiment the compound taken was in liquid form. The bond lengths which are less than the experimental values suggests that the carbon atoms (C7, C9 and C6) associated with two nitrogen and bromine atom in C1-C7, C3-C9 and C5-C6 respectively exert large attraction on the valence electron cloud of the carbon atoms C1, C3 and C9 due to their larger electronegativity. The bond lengths which are larger than the experimental values suggests that intermolecular hydrogen bonding (C-H...N) takes place in experimental unit of the titled compound. Also, the interatomic distance of two nitrogen atoms with bromine substituent of neighbouring molecules are reported to be 2.991Å and 3.099Å [14] which is considerably shorter than the sum of van der walls radii of respective atoms (3.40 Å). This indicates the presence of N....Br interactions [14].

The (C-C-C) bond angle lies between 119.09° - 121.35° and those of (C-C-H) lies between 120.06° - 120.84° and that of (C-C-Br) lies at 119.32°. The carbon atom appears to be a little distorted because of the intermolecular hydrogen bonding (C-H.....N) as seen from the bond angles (C6-C1-C7), which are calculated as 119.54°. Although there are differences, calculated geometrical parameters represent a good approximation and they can be considered as the basis of other calculations.

3.2. Vibrational Assignments

5-Bromobenzene1, 3-dicarbonitrile (BBDCN) is an aromatic nitrile containing a ring type of structure which has a dislocated π electron cloud. BBDCN with 14 atoms has 36 fundamental modes of vibration. Vibrational frequencies are calculated at B3LYP/6311 ++G(d,p) level of theory, since the B3LYP vibrational wavenumbers are known to be higher than those of experimental due to non-inclusion of anharmonicity effect and therefore an appropriate scaling factor 0.967 [15,16] is applied for a good agreement of calculated modes with the experimental modes. The calculated and scaled vibrational wave numbers and the detailed descryption of each normal mode of vibration of BBDCN carried out in terms of their contribution to the total potential energy are given in Table 2. The vibrational frequency assignments are made by using the result of VEDA 4 [13] program and Gauss View 5.0 program [12]. Theoretical IR spectra are plotted in Fig.2.

Table 2: Vibrational analysis of prominent modes of BBDCN at B3LYP/6-311++G(d,p) level of theory

Theoretical wavenumber(cm^{-1})	Scaled wavenumber (cm^{-1})	Assignment of dominant modes in terms of potential energy distribution (PED)
3213	3107	υ[(C2-H12)(69)+(C4-H13)(16)+(C6-H14)(15)]
3213	3107	υ[(C2-H12)(-30)] + υ[(C4-H13)(38) + (C6-H14)(31)]
3213	3107	υ[(C4-H13)(-46) + (C6-H14)(54)]
2343	2266	υ[(N8-C7)(44) + (N10-C9)(45)]
2342	2265	υ[(N8-C7)(45) + (N10-C9)(45)]
1628	1574	υ[(C4-C5)(20) + (C6-C5)(12) + (C2-C1)(15)+ (C3-C2)(25)] + β(H12-C2-C3)(13)
1591	1538	υ(C1-C6)(35) + β[(C4-C5-C6)(14) + (C3-C2-C1)(14)]
1451	1403	υ[(C4-C5)(12) + (C6-C5)(16)] + β[(H12-C2-C3)(24) + (C1-C6-C5)(13)]
1443	1395	υ[(C2-C1)(15) + (C3-C2)(23) + (C1-C6)(10)] + β[(H13-C4-C5)(11) + (H14-C6-C5)(11)]
1340	1296	υ[(C4-C5)(11) + (C2-C1)(11) + (C3-C2)(10)] + β[(H12-C2-C3)(14) + (H13-C4-C5)(21) +(H14-C6-C5)(21)]
1283	1241	β[(H14-C6-C5)(14) + (H13-C4-C5)(14)] +υ[(C6-C5)(15) + (C2-C1)(13) + (C3-C2)(16) +(C4-C5)(13)]
1266	1224	υ[(C1-C6)(10) + (C7-C1)(13) + (C9-C3)(13)]+ β[(C3-C2-C1)(19)]
1170	1131	υ[(C7-C1)(11) + (C9-C3)(11)]+β[(H12-C2-C3)(35)+(H13-C4-C5)(11) +(H14-C4-C5)(11) + (C2-C1-C6)(11)]
1132	1095	υ[(C4-C5)(20) + (C6-C5)(16)] + β[(C4-C5-C6)(13) + (H13-C4-C5)(20) + (H14-C6-C5)(20)]
1009	976	υ[(C1-C6)(17)]+β[(C4-C5-C6)(38)+(C2-C1-C6)(11)+ (C1-C6-C5)(13)]
940	909	υ[(C7-C1)(22) + (C9-C3)(22) + (C1-C6-C5)(21)]
931	900	ρ[(H13-C4-C5-C6)(46) + (H14-C6-C5-C4)(46)]
930	899	ρ[(H12-C2-C3-C4)(72) + (C3-C2-C1-C6)(12)]
900	870	ρ[(H13-C4-C5-C6)(27) + (H14-C6-C5-C4)(27)+ (C4-C5-C6-C1)(-17)]
816	789	υ[(C1-C6)(16) + (Br11-C5)(28)] +β[(C3-C2-C1)(10) + (C1-C6-C5)(16)]
689	666	ρ[(H12-C2-C3-C4)(21) + (H13-C4-C5-C6)(12)+ (H14-C6-C5-C4)(12) + (C4-C5-C6-C1)(10)+ (C2-C1-C6-C5)(10) + (C3-C2-C1-C6)(22)]
643	622	ρ[(N8-C7-C1-C2)(18)+ (N10-C9-C3-C2)(18)]+ β_{out}[(C9-C2-C4-C3)(28) + (C7-C2-C6-C1)(28)]
628	607	β[(N8-C7-C1)(-20)+(N10-C9-C3)(20)+(C7-C1-C6)(24)+(C9-C3-4)(24)]
572	553	ρ[(N8-C7-C1-C2)(13)+(N10-C9-C3-C2)(13)+(C4-C5-C6-C1)(16)]+β_{out}[(Br11-C4-C6-C5)(21)]
536	518	β[(C4-C5-C6)(10)+(N8-C7-C1)(24)+(N10-C9-C3)(24)+(C7-C1-C6)(14) +(C9-C3-C4)(14)]
463	448	υ[(C2-C1)(10) + (C7-C1)(14) + (C9-C3)(14)]+ β[(C3-C2-C1)(38)]
462	447	υ[(C7-C1)(16) + (C9-C3)(16)] +β[(C2-C1-C6)(39)]

428	414	ρ[(N8-C7-C1-C2)(24) + (N10-C9-C3-C2)(24)+ (C3-C2-C1-C6)(21)] + β_{out}[(Br11-C4-C6-C5)(16)]
380	367	ρ[(N8-C7-C1-C2)(19) + (N10-C9-C3-C2)(19)+ (C4-C5-C6-C1)(11) + (C2-C1-C6-C5)(37) +(C3-C2-C1-C6)(12)]
301	291	υ[(C1-C6)(10) + (Br11-C5)(63)]
272	263	β[(N8-C7-C1)(19) + (N10-C9-C3)(19) +(Br11-C5-C6)(50)]
176	170	ρ[(C4-C5-C6-C1)(28)+(C3-C2-C1-C6)(10)]+β_{out}[(Br11-C4-C6-C5)(39)]
161	156	ρ[(N8-C7-C1-C2)(12) + (N10-C9-C3-C2)(12)+ (C2-C1-C6-C5)(26)] + β_{out}[(C9-C2-C4-C3)(17)+ (C7-C2-C6-C1)(17)]
123	119	β[(N8-C7-C1)(13)+(N10-C9-C3)(13)+(C7-C1-C6)(15)+(C9-C3-4)(15)+ (Br11-C5-C6)(36)]
113	109	β[(N8-C7-C1)(19)+(N10-C9-C3)(19)+(C7-C1-C6)(26)+(C9-C3-4)(26)]
98	95	β_{out}[(Br11-C4-C6-C5)(17) + (C9-C2-C4-C3)(26)+ (C7-C2-C6-C1)(26)]

υ- stretching; β- in plane bending; βout-out of plane bending; ρ- torsion

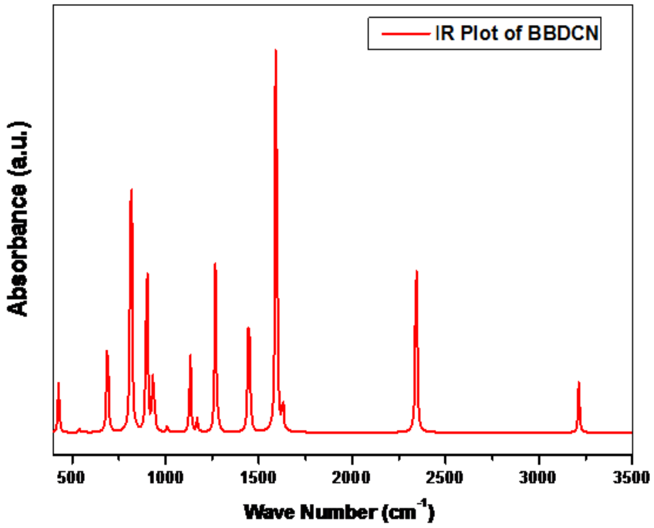

Fig. 2: Theoretical IR Spectra of BBDCN Molecule

3.2.1. C-H Vibrations

Generally the aromatic C-H stretching modes are found in the region 3100-3000cm^{-1}[17]. For the title compound the C-H stretching vibration are calculated in the range 3128-3011 cm^{-1}, which is in good agreement with the earlier reported values.

3.2.2. Phenyl Ring Vibrations

The title compound consists of a phenyl ring therefore the spectrum mainly involves bands corresponding to C-H, C-C, C=C and C-C-C and H-C-C bending as well as C-C-C-C torsion vibrations. The C-C ring stretching vibrations are expected within the region 1650-1200 cm^{-1} [18]. Most of these ring modes are influenced by the substitution to aromatic ring. The Calculated frequencies for C-C and C=C stretching modes at B3LYP/6-311++G (d,p) are reported in this communication at 1599 -1618 cm^{-1}, 1562 cm^{-1} respectively.

3.2.3. C≡N Vibrations:

The identification of C-N stretching vibrations is not an easy task due to possible mixing with other vibrations. As expected, the C≡N stretching modes with substantial contribution in PED in the case of BBDCN are found to be at 2343 cm^{-1}, 2342 cm^{-1}and match well with the values reported earlier [17].

3.2.4. C-Br Vibrations

C-Br vibrational modes with considerable contributions in PED are found in low frequency range at 816 cm^{-1} and 301 cm^{-1}which is in accordance with standard C-Br vibrations [17].

3.3. Electronic properties

In molecular interaction, two type of orbitals are formed known as Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO). These are also referred as frontier molecular orbital [19]. HOMO has an ability to donate an electron whereas LUMO has an ability to accept an electron. When two same sign of atomic orbitals overlap, electron density is occupied between the two nuclei. This molecular orbital is known as bonding molecular orbital resulting from in-phase interaction of atomic orbitals. These types of orbitals have lower energy than the original atomic orbitals. When two opposite signs of atomic orbitals overlap, or an out-phase interaction takes place, an anti-bonding molecular orbital with higher energy than the original atomic orbital is formed. The electronic reconfiguration and electronic excitations of frontier molecular orbitals are very much important for studying electrical and optical properties (such as whether the molecule is optically active or inactive) of the organic molecule. Energy difference between HOMO and LUMO is known as HOMO-LUMO band gap, which is an important feature for the stability of the molecule [19]. HOMO-LUMO band gap for BBDCN was found to be 5.138 eV. The 3D plots of the frontier orbitals, HOMO and LUMO for the title molecule are shown below in Fig 3.

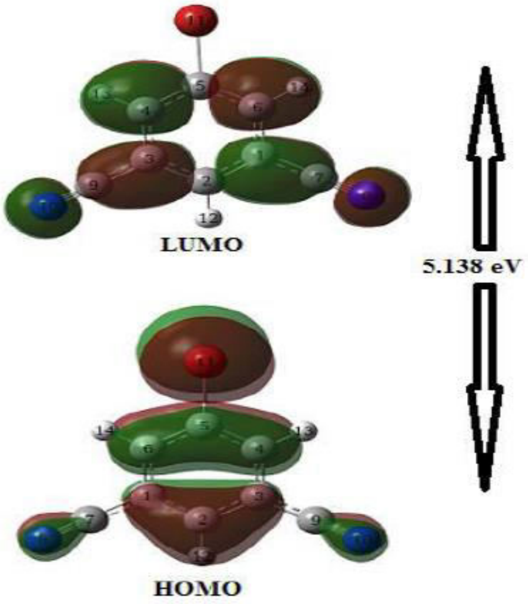

Fig. 3: HOMO-LUMO plot of 5-Bromoisophthalonitrile

In a molecule, charges are polarized rigorously in negative and positive terminals, due to which the electron density varies all over the molecule. This variation of electronic density can be viewed by molecular electrostatic potential map (MESP) [22, 28]. The MESP is used to study the electronic charge distribution of the molecule. Due to variation in charge densities, electrophilic and nucleophilic sites occur in a molecule. The red region in the map corresponds to the electrophilic reactivity *i.e.* a site of negative potential where an electron loving entity can attack while the blue region corresponds to the nucleophilic reactivity, a site of positive potential where an electron hating or proton loving entity can attack. MESP is also used for topographical analysis of the electronic structure. The MESP calculated at the B3LYP/6-311++G (d, p) for title molecule is shown in Fig 4.

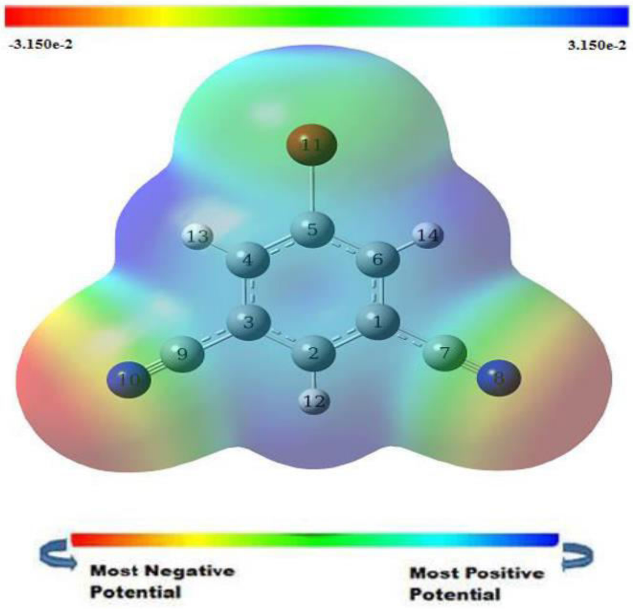

Fig. 4: MESP map of 5-Bromoisophthalonitrile

The molecular electrostatic potential map indicates that the negative region covers the nitride groups attached to the ring while the hydrogen attached to the ring possess the maximum amount of positive charges.

4. CONCLUSION

This communication on 5-Bromobenzene-1, 3-dicarbonitrile, comprises of geometry optimization, calculation of optimised parameters, bond length, bond angles and dihedral angles, by DFT (B3LYP) method and with basis set 6-311++G (d, p). The variations in calculated parameters with those of experimental ones have been discussed. In general, a good agreement between theoretical and experimental values has been observed. Vibrational analyses have been carried out and various modes of vibrations were explicitly assigned using the results of PED output obtained from the normal coordinate analysis. The molecular electrostatic map (MESP) of the compound under consideration have been calculated at same level of theory to understand the active sites of the molecule under study which shows that most of the region of the molecule is prone to be a nucleophilic centre and HOMO-LUMO band gap have also been reported to be 5.138 eV.

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